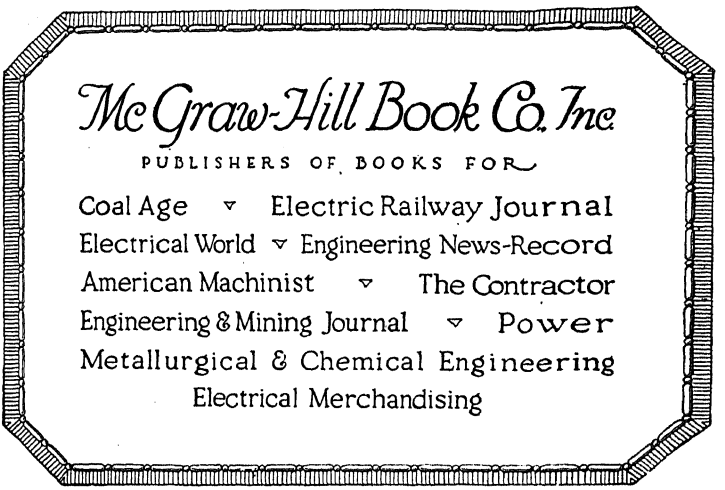

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THE HYDROMETALLURGY OF COPPER

BY

WILLIAM E. GREENAWALT, C. E., B. S.

PART I. ROASTING

PART II. HYDROMETALLURGICAL PROCESS

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PREFACE

The information available on the hydrometallurgy of copper is somewhat fragmentary and widely scattered. The wet methods, for treating copper ores, are diverse; as yet, the industry has not arrived at any established practice, and it is questionable, on account of the widely different character of the ores, if at any time one routine practice will succeed in eliminating other processes entirely. In the discussion of the various methods it is intended to cover all the most essential phases of the subject.

Roasting, both oxidizing and chloridizing, has been given a prominent place in the book, because on many ores, especially the sulphides, hydrometallurgical processes are directly or indirectly dependent upon this step for successful treatment.

The hydrometallurgy of copper differs from the hydrometallurgy of gold and silver largely on account of the greater percentage of material recovered. For this reason the discussion of the precipitation plays an important part. The commercial success of any particular process will frequently depend on the nature of the precipitant and the cost of precipitation.

The book is the result of notes, covering a long period of time, from various sources and from my own experimental work. It is intended, in the text, to give full credit for the various sources of information.

WILLIAM E. GREENAWALT.

DENVER, COLORADO,
August, 1912.

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THE HYDROMETALLURGY OF COPPER

PART I—ROASTING

CHAPTER I

PREPARATION OF THE ORE

Relation of Copper, Gold, and Silver.—Copper, gold and silver are chemically, mineralogically, and metallurgically intimately associated. Chemically, they occur in the same group in the Periodic System; mineralogically, one of these metals is rarely, if ever, found unaccompanied by one or both of the others; and metallurgically, any scheme which contemplates the profitable recovery of the copper must take into consideration the profitable recovery of the accompanying precious metals also.

In the hydrometallurgical treatment of copper ores, or of gold and silver ores containing copper, it is evident that the extraction of all three metals, concurrently or consecutively, must be given due consideration. Many operations in the wet treatment of ores of one of these metals are applicable to the others. In the acid treatment of gold and silver ores, as in chlorination, the conditions of roasting and extraction are not essentially different from the treatment of copper ores with acid solvents.

Many ores may be treated by hydrometallurgical processes without roasting. Others, especially the sulphides, have to be roasted, and the sulphides constitute the greater proportion of the available ores of copper. Some sulphides may be treated without roasting, but such treatment is the rare exception, and for obvious reasons will probably not find extensive application.

The best conditions of roasting, for the various ores for chemical treatment by any of the solvent processes, are very much the same, whether the metals to be extracted are copper, gold or silver, or all combined in the same ore. The same furnaces are used; the same costs apply; and the conditions of roasting which give the best extraction of the precious metals will, in general, also give the best extraction of the copper.

In roasting copper, gold and silver ores, for hydrometallurgical treatment, the metals themselves offer no particular difficulty in the operation. The difficulties encountered in roasting will usually be in the nature of

the other elements associated with them in the gangue. It is evident that in considering the roasting of copper ores, or copper ores containing gold and silver, the foreign elements must be taken into account quite as seriously as the metals themselves.

Roasting of ores, as a step for their treatment by solvent processes, is materially different from that required for subsequent smelting. While the chemical reactions during the roasting are essentially the same for both methods, a good roast for a solvent process requires vastly more delicate manipulation and a more thorough elimination of the sulphur. A roast which would be satisfactory for smelting might be, and usually is, absolutely worthless for treatment by wet methods; on the contrary, ore which is satisfactorily roasted for treatment by wet processes would be satisfactory for smelting also, but the expense of roasting would be considerably greater.

In ores containing copper, gold and silver, if the precious metals are not extracted simultaneously with the copper, the roasting of the ore to make their subsequent extraction satisfactory, either by cyanidation or chlorination, must be taken into account.

Cupriferous pyritic ores, high in sulphur, are sometimes roasted in heaps, preparatory to extracting the copper as soluble sulphate, but this practice is not finding extended application, and at the mine where it was largely employed its use has been discontinued.

The only roasting which is finding favor for the hydrometallurgical processes is in suitable furnaces, usually reverberatories, and preparatory to which the ore is crushed fine enough to be thoroughly roasted in several hours.

Preparation of the Ore.—Ore, as roasted in furnaces for hydrometallurgical treatment, is usually crushed to a fineness varying from 8 to 40 mesh. Below 8 mesh the particles become too large for efficient oxidation, and above 40 mesh the dust is likely to give trouble. On the whole, ore ground to a fineness varying from 10 to 30 mesh will give the best average results.

When roasting constitutes a step in any metallurgical process, the ore is crushed dry. Rolls and ball mills are best suited for this work. Concentrates are usually the product of wet crushing. If the ore is of too low a grade to admit of direct chemical treatment, concentration offers a means of increasing the tenor of the material, while at the same time eliminating the most injurious elements. In this way, lime particularly may be largely eliminated from the ultimate product to be treated by roasting and a chemical process. If concentration forms a step in the general treatment, there is no need of close work to obtain a high grade concentrate, and hence there is no need of excessive loss in the tailings. A concentrate containing 10 per cent. copper would be a very desirable product for roasting and for treatment by a solvent proc-

ess, and such a concentrate should be made without excessive loss; whereas if shipment to a smelter is desired, such a product would not present much advantage, and to get a higher grade product would result also in getting a considerably greater loss.

The moisture contained in the ore before charging into the furnace should also be considered. Concentrates may be charged in a hand-rabbled furnace without drying, but in mechanical roasters it is evidently better to remove the moisture sufficiently so that the ore may be fed uniformily into the furnace by mechanical means. Much moisture in the ore charged into the furnace has a tendency to cool it unduly.

The moisture in the ores, as well as the moisture in the fuel gases, has an important bearing on the chemistry of the roasting process.

The principal expense in the preparation of the ore for roasting is in crushing. This may vary within wide limits, depending on the character of the ore, the fineness to which it is reduced, and the amount crushed. Usually it will vary from 25 to 50 cents per ton, with a reasonably large installation.

Dry Crushing with Rolls.—Rolls are largely used to crush ore to medium fineness. For grinding finer than 20 mesh they are inferior to some other type of machines, and it is a question whether, under any conditions, they are as satisfactory as ball mills.

It costs from 25 to 30 cents per ton to crush Cripple Creek ore to 12 or 14 mesh, on a basis of from 200 to 300 tons per day. In one plant, having two 48-in. roughing rolls and four 48-in. finishing rolls, 300 tons of ore are regularly crushed per day. The roughing rolls are run only during the daytime, but the finishing rolls are run continuously for three eight-hour shifts, with three men on a shift. One man attends to the screens.

In another plant, having one 36-in. roll, and three 26-in. rolls, 175 tons are crushed in 24 hours to from 30 to 40 mesh.

A combination of one 36-in. roughing roll; one 26-in. roll doing medium work, and two 26-in. rolls doing finishing work, will crush from 125 to 175 tons of ore of ordinary hardness to 30 mesh; 200 to 250 tons to 20 mesh, and 250 tons and more to 16 mesh.

For the best working of a roll crushing plant, it is essential that the reduction shall be gradual in going from one roll to the next.

Dry Crushing with Ball Mills.—For dry crushing ball mills present certain advantages over rolls in that they are self-contained and the screening is simplified. Their capacity is also large. A No. 5 Krupp ball mill will crush 43 tons daily of ordinary sulphide ore, and the No. 8, 100 tons; using from 18 to 23 h. p. for the 5-ton mill, and from 60 to 65 for the 8-ton mill, or 2.1 and 1.6 tons per horse-power respectively.

M. W. Von Bernewitz[1] has given some valuable information on ball

[1] *Min. and Scientific Press*, July 15, 1911.

mill practice at Kalgoorlie. The following table gives a summary of the essential facts.

BALL MILL PRACTICE AT KALGOORLIE (DRY CRUSHING)

Name of plant	No. of mills	Weight of balls	Screen	Speed	Power	Capacity daily	Steel consumption	Life of grinding plates
		lb.		r. p. m.	h. p.	tons	lb. per ton	days
Associated	4 No. 8	4480	30×30	21	60	92–95	0.50	170
	6 No. 5	2240	25×25	25	23	43		
Associated Northern	3 No. 5	2350	27×27	26	18	40	0.32	270
Chaffers	3 No. 5	2300	27×27	25	25	40	0.74	180
Great Boulder	4 No. 8	4480	30×30	24	60	80–90	0.64	105
Kalgurli	9 No. 5	2200	26×26	25	25	40	0.45	300
Perseverence	8 No. 8	4400	27×27	24	60	100	0.65	118
South Kalgurli	3 No. 8	4480	27×27	24	65	95–100	0.47	210
	1 No. 5	2800			30			

COST OF CRUSHING AT KALGOORLIE, PENCE PER TON

Name of plant	Wages	Power	Other items	Total	
				Pence	Dollars
Associated	6.45	13.78	9.89	30.11	0.574
Associated Northern	5.87	12.08	6.25	24.22	0.463
Chaffers	2.09	10.64	8.84	21.57	0.413
Great Boulder	1.81	9.75	6.26	17.82	0.342
Kalgurli		15.23	7.49	22.72	0.435
Perseverence	3.21	19.18	4.43	26.84	0.514
South Kalgurli	2.05	20.82	9.43	32.20	0.619

One man per shift of 8 hours, at 11s. 8d. ($3.22) can look after eight No. 8 ball mills; but in smaller plants the mill man attends to conveyors, elevators, dust, pipes, etc. Ball mills should be fed with no larger ore than will pass a 3-in. ring. With fine ore the balls are likely to bed. Actual weighing has shown a 3-in. feed is crushed faster and the wear of steel is less than when 1-in. material is fed with a quantity of fines.

A No. 5 mill, including foundations, may be erected for £600 ($2922.00) and a No. 8 for £1000 ($4870.00), bin and conveyor included. It will usually cost about £300 ($1461.00) per year for upkeep of a No. 5.

At the Golden Cycle mill, at Colorado Springs[1] four No. 66 "Kominuters" have à capacity of 17,000 lb. of Cripple Creek ore per hour for each mill, when fed with a product that had been reduced by rolls to pass through a revolving screen made of 1/4 in. steel plate and having openings 1 1/2 in. in diameter. The kominuters were equipped with

[1] Lochiel M. King, *Mining and Scientific Press*, Jan. 25, 1908.

a diagonal slotted screen, size of opening 5/32 by 1/2 in. No. 8 steel plate. This opening gave a product varying in size from 1/8-in. cubes to the finest slimes. The consumption of power was 50 h. p. at a speed of 22 r. p. m., the ball consumption being fourteen 5-in. forged steel balls weighing about 19.5 lb. each, per day of 24 hours. One man can attend to six mills.

The average results from several types of ball mills show that one ton of steel balls will crush about 50 tons of ore during 24 hours from a feed 1 1/2 in. diameter down to a product of from 12 to 20 mesh in one operation.

CHAPTER II

FUEL

Roasting, as a step in the treatment of ores by the hydrometallurg processes, is usually carried out in the immediate vicinity of the mi At industrial centers, the consideration of fuel is a very simple mat but not so in copper, gold and silver mining districts where the selec of a particular kind of fuel is frequently a matter of necessity, basec local conditions. In vicinities where wood is abundant it will ordina be used in preference to the more expensive coal, which has to be freigh in. If a mining district has no wood, and is some distance from source of fuel supply, the greater calorific power of oil per unit of we over that of the coal might make it the cheaper fuel on account of difference in cost of freight.

Other things being equal, the relative desirability of fuels for ro ing purposes is gas, oil, bituminous coal, wood, lignite. Anthracit not often available, but if it is, there is a decided advantage in converging it into producer gas.

Most of the expense of roasting, in mechanical furnaces, is in fuel. Some of the essential facts pertaining to the various fuels ar comparison of their relative value is, therefore, pertinent.

Wood.—It frequently happens that in mining camps far remo from coal supply, wood can be obtained cheaply and in large quanti For roasting, if the wood is perfectly dry, it is more desirable t lignite of the inferior qualities of bituminous. Green wood cont from 30 per cent. to 40 per cent. moisture. After thorough season for about a year, in the open air, the moisture is from 20 to 25 per c

The wood of various trees are nearly identical in chemical comp tion, which for perfectly dry wood and of ordinary fire wood hol hygroscopic moisture, is practically as shown in the table on the foll ing page.

The ash in most woods varies from 0.5 to 1.5 per cent. Most of pines and others of the coniferous family contain hydrocarbons (pi turpentine) which increase their value as fuel.

In steam-boiler tests wood is assumed as 0.4 of the value of same weight of coal. It is safe to assume that 2 1/4 lb. of dry-woo equal to 1 lb. of average quality bituminous coal, and that the value of the same weight of different woods is nearly the same. T is to say, a pound of pine is worth as much for fuel as a pound of hick supposing both to be dry.

	Dessicated wood	Ordinary fire wood
Carbon	50 per cent.	37.5 per cent.
Hydrogen	6 per cent.	4.5 per cent.
Oxygen	41 per cent.	30.75 per cent.
Nitrogen	1 per cent.	0.75 per cent.
Ash	2 per cent.	1.5 per cent.
	100 per cent.	75.0 per cent.
Hygroscopic water		25.0 per cent.
		100.0 per cent.

It is important that the wood be dry, as each 10 per cent. of moisture in wood will detract 12 per cent. from its value as fuel.

A cord of wood is a pile 4 ft. by 4 ft. by 8 ft. which is equal to 128 cu ft. About 56 per cent. is solid wood, and 44 per cent. spaces.

Fire-boxes for burning wood should be built so as to contain a deep bed of fuel. They should be narrower at the bottom than at the top With properly designed fire-boxes, burning thoroughly dry wood, a very intense heat can be obtained which is quite as effective in roasting ores as most coals available in copper mining districts.

Where wood is abundant in the Rocky Mountain Region it will ordinarily cost from $3.00 to $3.50 per cord, cut and piled at the metallurgical works ready for use.

Wood burns with a long flame and makes comparatively little smoke which are ideal conditions for roasting.

Charcoal gives out much more useful heat than wood, because the water contained in the wood, or formed by the combustion of its oxygen and hydrogen, has to be evaporated during its combustion. 100 parts of wood give only as much heat as 40 parts of charcoal.

Charcoal is made by the dry distillation of wood, at a temperature of from 460° to 450° C. This may be done in heaps or in closed retorts Dry wood in stacks yields about one-fourth its weight in charcoal Charcoal develops on burning 8000 heat units, while wood, dried in the air, does not develop more than 2800 units of heat. Therefore, seven parts of charcoal gives as much heat as 20 parts of wood, but the 20 parts of wood are capable of yielding only five parts of charcoal.

If wood has to be transported any considerable distance for roasting it might be profitable to convert it into charcoal at the forests and then

RELATIVE HEATING VALUE OF WOOD, COAL, AND OIL

One cord of wood (128 cu. ft.)	Weight in pounds per cord	Pounds of coal equivalent to one cord of wood	Pounds of oil equiv to one cord of wo
Hickory	4,500	1,800 to 2,000	1,000
White Oak	3,850	1,540 to 1,715	860
Beach, Red Oak, Black Oak	3,250	1,300 to 1,450	725
Poplar, Chestnut, Elm	2,350	940 to 1,450	525
Pine	2,000	800 to 925	460

It might be said that the approximate heating value of wood, and oil is: 2 cords of average pine = 1 ton of average bituminous co 1 3/8 tons of lignite = 3 1/2 to 4 barrels of crude oil.

As to the absolute consumption of fuel, in roasting, much dep on the nature of the ore, the amount of sulphur in the raw ore, and extent to which the sulphur is eliminated.

Oil.—Oil, next to gas, is the most desirable fuel for roasting purp It is largely used where it can be obtained cheaply and the supp constant. It was for many years the principal fuel used in roas Cripple Creek ores. Recently, owing to the uncertainty of the sup producer gas has largely displaced the crude oil and residuum. California, where large oil fields have lately been developed, it is placing wood and coal in the roasting of stamp mill concentrates chlorination.

Fuel oil has the following advantages over coal and wood in roas ores:

Reduction of weight of fuel by 50 per cent.

Reduction of bulk of fuel by 30 per cent.

Reduction of labor by 50 per cent.

Prompt kindling of fire.

Cleanliness and freedom from ash.

No loss of heat by useless radiation, as in the coal fire-box w the heat and products of combustion are introduced through the to the arch.

Convenience in directing and controlling the heat.

It is possible to get with it either a long rolling flame, or an inten hot local flame.

Oil, as it is used in roasting ores, is sprayed with a steam jet dire

Most of the oil sold for fuel purposes ranges from 14° to 20° Baume. Oil is usually bought by measure and not by weight. The lighter gravity oils contain more heat units per pound than the heavier oils, but there are more pounds of fuel in a gallon of heavier oils than in a gallon of lighter oils. The gravity of the oils, therefore, is not a matter of much consequence.

A U. S. gallon of oil weighs from 6.5 to 7.2 lb. and 42 gallons are taken as a barrel. Residuum, that is, the residue of crude oil after the volatile substances have been driven off by heating, is largely used as fuel for roasting purposes.

In some of the mills treating Cripple Creek ore both coal and oil are used in the same furnace. In some of the roasting furnaces coal is used at the cooler, or feed end, while in others the reverse is the case. The relative quantity of coal and oil used also varies greatly. The average consumption might be considered as 100 lb. of coal and 15 gallons of oil per ton of ore, in roasting 1 1/2 to 3 per cent. sulphur down to about 0.5 per cent. With oil alone, it takes from 0.35 to 0.45 barrels to roast a ton of ore, in addition to the small amount of fuel necessary to generate the steam for applying the oil.

In California it takes about half a barrel of oil to roast a ton of stamp mill concentrates suitable for chlorination, and about 50 lb. of coal to furnish the steam to pump, heat, and atomize the oil. As a fuel 90 gallons of California oil is equal to 1 ton of coal.

If fuel has to be transported any considerable distance, oil offers advantages in the cost of freight, since for the same weight it has about twice the heating value of coal, and about four times that of wood.

Coal.—Coal is the most universally used fuel in roasting. Its quality, however, varies so much that careful investigation of the different kinds available is a serious matter. A long-flame bituminous coal, if direct firing is used, is the best, while lignite, with its short flame and low heating quality, is the worst. The tendency of short-flame coal is to give an intense local heat, and such a heat is highly detrimental to the roasted ore. The best way to distribute the heat is either to gassify the coal, or if fired direct, get what is known as a semi-producer action in the fire-box, by the introduction of steam and air under the grate. By either of these methods, a long rolling flame may be obtained in the roasting chamber.

Any coal, whether anthracite, bituminous, or lignite, will give the most satisfactory result by being first converted into producer gas, and conducting the gas from the producer mains into the different parts of the furnace, and there consuming it, so that the atmosphere shall be

The advantages of producer gas over direct firing are:

The gas may be produced from inferior coal, and makes more available heat in the roasting furnace than is possible with any coal burned in an ordinary grate.

It can be easily introduced into the roasting furnace at any point and in any quantity desired, thereby giving a diffused heat over the entire bed of the ore.

The construction of the arch of large mechanical furnaces is very much simplified.

The producers may be centralized, so that the handling of coal and ashes, by mechanical appliances, may be greatly facilitated.

In all cases, where producer gas is used to roast ore, the air necessary for its combustion should be pre-heated. This can be done at the least expense by an air-heating arrangement in the furnace dust chamber.

The relative average value of the several classes of coal may be approximately determined from the accompanying tables.

CLASSIFICATION OF COALS
(Kent, *Min. Ind.*, 1900)

	Moisture per cent.	Ash per cent.	Volatile matter per cent.	Fixed carbon, per cent.	Heating value b. t. u. per lb. of combustible	Relative value of combustible semi-bit. =100
Anthracite and semi-anthracite.	1 to 3	8 to 12	3 to 12	97 to 88	14,700 to 14,900	94
Semi-bituminous.....	1 to 3	3 to 10	15 to 25	75 to 85	15,600 to 16,000	100
Bituminous—eastern.....	1 to 3	3 to 15	25 to 40	60 to 75	14,800 to 15,200	95
Bituminous—western.....	4 to 14	5 to 25	35 to 50	50 to 65	13,600 to 14,800	90
Lignite.....	12 to 18	5 to 25	over 50	Less than 50	11,000 to 13,000	76

A rough estimate of the relative practical value of the several classes of coal may be calculated as follows:

	Moisture %	Ash %	Combustible %	b. t. u. per lb. combustible	Theortical healing value	Efficiency for boiler	Relative practical value	
							b. t. u.	Semi-bit. =100
Anthracite	2	13	85	14,800	12,180	77	9,379	88
Semi-bituminous	2	8	90	15,800	14,220	75	10,665	100
Bituminous—eastern	2	8	90	15,000	13,500	70	9,450	89
Bituminous—western	10	15	75	14,200	10,150	65	6,598	62
Lignite.....	15	20	65	12,000	7,800	60	4,680	44

Heating value per pound in b. t. u. equals:

$$1/100[14{,}650C + 62{,}000\left(H - \frac{O}{8}\right) + 4000S]$$

In which C, H, O and S are respectively the precentages of carbon, hydrogen, oxygen, and sulphur in the coal.

There is more ash in the smaller size coal than in the larger sizes, due principally to the greater quantities of dirt and slate, as shown by the following analyses of different sizes of anthracite.

Size of coal	Fixed carbon	Ash
Egg, 2.5 to 1.7 in.	88.5 per cent.	5.7 per cent.
Stove, 1.75 to 1.25 in.	83.7 per cent.	10.2 per cent.
Chestnut, 1.25 to 0.75 in.	80.7 per cent.	12.7 per cent.
Pea, 0.75 to 0.50 in.	79.0 per cent.	14.7 per cent.
Buckwheat, 0.50 to 0.25 in.	76.9 per cent.	16.6 per cent.

CHAPTER III

OXIDIZING ROASTING

Objects of Roasting.—The object of roasting is to convert the into a condition which will have the least injurious effect on the ch icals used, and to simplify their application. Roasting is essenti oxidation. Many metallic oxides are not as readily attacked by solvent in the subsequent chemical treatment as the metals in o combinations.

The solvents for copper, gold and silver are among the most e getic substances known. Chlorine, for example, combines with t elements with which oxygen is able to combine, because in many resp it is equally if not more energetic than oxygen, and replaces it in proportion of 2 atoms of chlorine to one of oxygen: Cl_2: O. Chlo cannot displace oxygen from many of its oxide combinations. is universally associated with copper, gold and silver ores in the f of oxide or sulphide. Chlorine very rapidly combines with iron in sulphide and sulphate combinations, but does not appreciably disp the oxygen from its oxide combinations. Most of the metals less injurious in their oxide than in their sulphide combinations, w others are not much improved by the change. If the ore is to treated for its copper content by an acid process, the oxide of cop resulting from the roasting is readily soluble in either hydrochl or sulphuric acids, while the sulphide of copper is quite insolubl either of these acids. Calcium is acted upon by chlorine and acids as readily in its oxide as in its carbonate combinations. M of the calcium, however, in roasting, is converted into the sulph which is an improvement, since it is practically neutral and unaffe by all solvents.

Many injurious metals, such as arsenic, antimony, and bismuth, volatile at a high temperature and are expelled during the roast Many oxides are benefited by elevated temperatures. Dehydrat agglomerates the particles and makes a better leaching product. C containing much clay and talc are similarly benefited. And, fina roasting makes the ore particles porous, thereby very materially incre

The objects of roasting, therefore, may be summarized as follows:

1. To oxidize. The common elements oxidized are iron, copper, lead, zinc, aluminum, calcium and magnesium.

2. To volatilize. The common elements volatilized are sulphur, arsenic, antimony, bismuth and tellurium.

3. To sulphatize. The common elements sulphatized are calcium, magnesium and, to some extent, lead and zinc.

4. Dehydration. The object of dehydration is to agglomerate the ore particles and make them more susceptible to leaching, decantation, or filtration. Usually ore, which will percolate or filter very slowly before roasting, will percolate or filter quite rapidly after roasting. Mill dust, when raw, may be difficult to filter, but after roasting filtration takes place quite rapidly.

5. To make the ore porous. Oxidation of sulphide and telluride ores, by the elimination of the sulphur and tellurium, must of necessity make the ore particles more porous and present a greater surface to the action of the solvent. Most ores will yield a very much better extraction after roasting than before, even though they are otherwise equally susceptible to treatment.

6. To free the gold and silver particles. Neither chlorine nor cyanide are practical solvents of gold and silver in their telluride combinations, and in their sulphide combinations they present serious difficulties. After roasting, the gold and silver are in their metallic state and are readily soluble if the particles have not been fused.

7. To convert the desired metals into soluble form. Copper, in its sulphide combinations, is quite insoluble in either acid or alkaline solutions, while in its oxide combinations it is readily soluble.

Chemical Combinations of the Metals before Roasting.—Copper, gold and silver ores as they come from the mine, may contain any of the base elements. The matrix is almost always quartz, but associated with it will usually be found one or more of the elements enumerated:

Aluminum; usually as a silicate, fluoride or sulphate.

Antimony; usually as a sulphide.

Arsenic; usually as a sulphide.

Barium; usually as a sulphate or carbonate.

Calcium; usually as a carbonate, fluoride, or sulphate.

Cobalt; usually as a sulphide.

Copper; usually as a sulphide, carbonate, oxide or silicate.

Iron; usually as a sulphide, carbonate, or oxide.

Lead; usually as a sulphide or carbonate.

Magnesium; usually as a carbonate.

Zinc; usually as a sulphide or carbonate.

Sulphur and tellurium are usually found in combination w metals as sulphides and tellurides.

General Chemical Reactions During Roasting.—The carbona heating, are readily converted into the oxides of the metals and dioxide:

$$MCO_3 = MO + CO_2.$$

When metallic sulphides are heated in the presence of air, oxides and sulphur dioxide are formed:

$$MS + O_3 = MO + SO_2.$$

Most of the sulphur dioxide passes off, but a small portion converted into sulphur trioxide by contact with the metallic formed, or with the silica contained in the ore:

$$SO_2 + O + SiO_2 = SO_3 + SiO_2$$
$$SO_2 + 2MO = SO_3 + M_2O.$$

Some of the sulphur trioxide will escape, while some will c with the metallic oxides to form metallic sulphates:

$$MO + SO_3 = MSO_4.$$

By heating, the metallic sulphates are dissociated, some giv sulphur trioxide, others sulphur dioxide and oxygen:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$
$$2CuSO_4 = 2CuO + 2SO_2 + O_2.$$

The sulphates of copper, antimony, iron, and nickel, are com decomposed at a red heat. A higher temperature decompos sulphates of aluminum, silver, lead, manganese, and zinc. An o white heat has no action on the sulphates of the alkalies and a earths, potassium, sodium, barium, calcium, and magnesium, but most intense heat procurable, which is never used in a roasting f the sulphates of barium and calcium are changed to oxides. same temperature, sodium and potassium sulphates are com volatilized.

Essential Factors in Roasting.—The essential factors in roasti

Time,
Temperature,
Air, or Oxygen.

These are complementary terms, and each may be carried in to the neglect of the others. Roasting, as already stated, is su tially oxidation by the application of heat and air. Mineralized ve oxidized to great depths by time and the action of atmospher

abundance of air, is of little avail. A moderate temperature, with an abundance of air, is highly efficient, nevertheless time is necessary to effect complete oxidation, and to get the best roast for subsequent chemical treatment to extract the metals.

Time.—Time in roasting, and in oxidation, is a most variable factor. Pyrites may be oxidized almost instantly, in the highly oxidizing atmosphere of a shaft furnace, or it may take countless ages, as in the oxidation of mineralized veins, where the elements of both temperature and air are lacking.

Some idea of the relation of time, temperature, and air may be obtained from roasting tests made in Denver, on Gilpin County sulphide ore. The ore was roasted in a three-compartment shaft furnace at the rate of 75 tons a day. Each particle was exposed on all sides to a highly heated oxidizing atmosphere. The ore was thoroughly roasted in 1 3/4 minutes, which was the total time it remained in the furnace. Similar ore was roasted in a mechanical reverberatory, with a bed from 4 to 5 in. deep, and notwithstanding that the ore was rabbled continuously and remained in the furnace from 4 to 5 hours, the roast was not satisfactory. The difficulty lay in the inability of the air to penetrate the deep bed of ore. As soon as an abundance of air was supplied, as for example, when the ore was discharged from the furnace, innumerable sparks appeared, showing that the oxidation was taking place more rapidly.

In the Stedefeldt shaft furnace the ore is oxidized almost instantly, and the time reduced to a minimum, as compared with roasting in the ordinary reverberatory or revolving furnaces. In the Stedefeldt furnace, which was used only for chloridizing roasting silver ores, the chlorine acted as an energetic oxidizer, and this materially assisted in the roasting.

The best results in roasting will usually be obtained when the time factor is made as great as possible, and the temperature as low as possible, assuming that the air factor remains the same. Or, again, the best results will always be obtained by having the time and air factors as large as possible, speaking, of course, within practical limits. By increasing the air, the temperature remaining the same, the time will be greatly diminished without detriment to the roast.

If ore is roasted, as in a shaft furnace of the Stedefeldt type, where it is showered through a highly heated oxidizing atmosphere, the time of roasting is reduced to a minimum, but the combustion of the pyrite is likely to be so intense that the heat developed in the particle itself is likely to fuse it. Careful panning of roasted sulphide ore, roasted under such conditions, will usually disclose some of the grains as fused or even

Temperature.—The regulation of temperature in a furnace to ge best results in roasting, depends largely on the nature and compos of the ore. In simple ores, not containing too much sulphur, slow i heating is not essential if care is taken not to carry the heat too nea sintering point. Even on concentrates, and ore high in sulphur, initial heat may be reasonably high without deleterious effects, prov there is an abundance of air and the rabbling in sufficiently frequ Copper sulphides are vastly more sensitive to high temperatures iron sulphides, and with galena, which fuses at a low temperature utmost care must be taken.

When roasting silicious ore in large furnaces, or even pyritic mat containing only small quantities of copper or lead sulphides, the rea may be pushed quite as hard as the first one, since the temperatu the ore must be brought to the ignition- or to the volatilization-poi sulphur, before roasting can begin. This fact was demonstrated interesting experiments made in roasting Cripple Creek gold ore, in 100-ton furnaces. Three of these furnaces were of the ordinary chanical reverberatory type; the fourth had a revolving hearth, wi gas producer in the center, and which was so fired that the tempera throughout the entire hearth was practically the same. The raw entering the furnace was subjected to almost the same heat as roasted ore being discharged. A comparison of several thousand of tailings from the different furnaces showed no material differen the extraction.

The ordinary roasting starts with a low initial heat, and finish the highest temperature the ore will stand without sintering. Th particularly true of all revolving furnaces, and to a large extent in re beratories also. While this may be the best for some ores, careful c parative tests in large furnaces would indicate that it is better to b the ore as quickly as possible to a dull red (or even cherry red) heat, that the finishing temperature should not be too high. In roasting containing from 2 per cent. to 4 per cent. sulphur, in a furnace ha say four fire-boxes and roasting 100 tons per day, the best results wi obtained by firing the finishing fire box at a lower temperature than one preceding it. The dark magnetic oxide is, to a large extent, verted into the ferric oxide by the prolonged roasting at a modera low temperature. Similarly the cuprous oxide, which is with s difficulty soluble in acids, may be reduced to the cupric oxide, whi quite readily soluble.

If the ore is overheated, as is frequently the case when the finis heat is high, it will have a dark appearance; whereas, if finished

oxide, which, at a lower temperature and with an abundance of air, may be reconverted into ferric oxide.

In order to determine the effect of temperature on the extraction, the following laboratory experiments were made on Cripple Creek ore. Chlorine was used as the solvent. Head assay of raw ore, gold 5.32 oz.; head assay of roasted ore, gold 5.56 oz.; sulphur in raw ore, 4.02 per cent.

Test No. 1.—The ore was given what appeared to be an ordinary roast in an assay muffle. The finishing heat was that ordinarily given in large furnaces. The ore did not show any sintering. Sulphur in roasted ore, soluble, 1.16 per cent.; insoluble, 0.26 per cent.; total, 1.42 per cent. Average tailing from 10 bottle tests, 0.50 oz. Extraction, 91 per cent.

Test No. 2.—The ore was given a prolonged roast to reduce the sulphur content. The finishing heat was quite high (about 1575°F.) but the ore was not sintered. Sulphur in roasted ore, soluble, 0.90 per cent.; insoluble, 0.10 per cent.; total, 1.00 per cent., Average tailing from 10 bottle tests, 0.33 oz. Extraction, 94 per cent.

Test No. 3.—The ore was roasted at a high heat, and finished at a very high temperature (about 1650 to 1700° F.); it had a dark appearance and was slightly fused. Sulphur in roasted ore, soluble, 0.34 per cent.; insoluble, 0.09 per cent.; total, 0.43 per cent. Average tailing from 10 bottle tests, 1.23 oz. Extraction, 78 per cent. Two bottles were recharged and treated 12 hours; recharge tailings ran 0.79 oz. Extraction, 86 per cent.

Test No. 4.—The ore was roasted 10 hours in the muffle. It was brought quickly to a red heat, and finished at a moderately high temperature. The ore had a dark appearance, and the finer particles were slightly fused. Sulphur in roasted ore, soluble, 0.75 per cent.; insoluble, 0.11 per cent.; total, 0.86 per cent. Average tailing from 10 bottle tests, 0.73 oz. Extraction, 88 per cent.

From Tests 3 and 4 it is evident that if the ore is fused or sintered, a close extraction is impossible.

Test No. 5.—The ore was roasted 5 hours at a very low temperature (scarcely visible red); it was taken out of the muffle and divided into two parts. One half was returned to the muffle and roasted 8 hours longer at a low dull red heat. The finishing heat was a dull red. The entire roasting was performed at a prolonged low temperature. Sulphur in roasted ore, soluble, 0.74 per cent.; insoluble, 0.25 per cent.; total, 0.99 per cent. Average tailing from 10 bottle tests, 0.15 oz. Extraction, 97.3 per cent.

Test No. 6.—The other half of the ore taken from No. 5, after roast-

total, 0.93 per cent. Average tailing from 10 bottle
Extraction, 91 per cent.

In the bottle tests for the different roasts, the condi
the same. The chemicals corresponded to 15 and 20 lb
30 and 40 lb. of sulphuric acid, per ten of ore. The tim
on account of the high grade of the ore, was 5 hours. The
to 16 mesh.

It will be noticed that the best results were obtain
where the finishing heat was quite low. By increasin
extraction was not improved, as shown by No. 6. In No
not roasted sufficiently, as indicated by the sulphur
per cent. In No. 3 the ore was roasted at too high a te
sulphur content is low, 0.43 per cent. The sulphur in
more nearly the mill roast. For ore having 4 per cen
soluble and insoluble sulphur in the roasted ore, as repr
2, might be considered normal for Cripple Creek ore
heat, as represented by No. 5, will give the best aver
The conditions there represented, however, could proba
realized in practice, on account of the reduced capacity

These test were repeated in large furnaces roasting
daily, and each test represents a day's run, or 200 tons.
is based on the mill tailings. Furnace No. 1 was fired
heat and a higher finishing heat. Furnace No. 2 was fire
initial heat and a lower finishing heat. Care was taken
possible roast under both conditions.

FURNACE TEST NO. 1

		Furnace No. 1	F
Sulphur, raw ore,		2.75 per cent.	2
Sulphur in roasted ore,	soluble,	0.75 per cent.	0
	insoluble,	0.09 per cent.	0
	total,	0.84 per cent.	0
Assay of roasted ore, gold,		1.05 oz.	1
Assay of chlorination tailings,		0.08 oz.	0
Extraction,		92.4 per cent.	94

FURNACE TEST NO. 2

Sulphur, raw ore,		2.66 per cent.	2
Sulphur, roasted ore,	soluble,	0.71 per cent.	0
	insoluble,	0.07 per cent.	0
	total,	0.78 per cent.	0
Assay of roasted ore, gold,		1.23 oz.	1
Assay of chlorination tailings,		0.12 oz.	0
Extraction,		90.0 per cent.	94

These comparative tests in actual mill practice, in fu
100 tons of ore per day, are characteristic of many oth

the same lines. The results clearly indicate that the lower finishing heat gives the best average results; that ore roasted at a low temperature gives up its values better than ore roasted at a high temperature, and that sintering or overheating is highly injurious. The ore in these tests was ground to 10 mesh. Time of chlorination, 3 hours. The chemicals used were 15 lb. of bleach and 30 lb. of sulphuric acid, per ton of ore.

Valentine's Temperature Experiments.—Valentine[1] made interesting experiments on the effect of temperatures on iron pyrite, with and without free access of air. The results of his experiments undertaken to ascertain the effect of heat on FeS_2, when air is freely given access, are given as follows:

Approximate temperature, deg. F.	Duration of heat	S. in residue, per cent.	Loss, per cent.	Per cent. of S. expelled
Original pyrite		53.43		
1250	1 hour	4.27	49.15	92.05
1250	2 3/4 hours	0.70	52.73	98.68
1600	20 minutes	0.78	52.65	98.54
1600	45 minutes	0.08	53.35	99.85
1800	20 minutes	0.13	53.29	99.75
1800	1 hour	0.65	52.78	98.79
2200	15 minutes	3.23	50.19	93.95
2200	20 minutes	5.92	47.51	88.93
2200	35 minutes	1.56	51.87	97.10
2200	2 hours	1.18	52.24	97.78

It will be noticed that a larger amount of sulphur remains in the residues when higher temperatures have been applied.

Valentine, from his experiments, draws the following conclusions in roasting pyritic ores:

1. Heat alone without access of air, can remove at best only one half of the sulphur present.

2. Atmospheric oxygen is absolutely necessary for a proper desulphurization.

3. Even at a low heat, ore is properly desulphurized if air can gain access freely to the FeS_2 in it.

4. Sulphate of iron can be decomposed equally well with or without air.

5. In order that the residuum sulphur in roasted ore may consist as far as possible of sulphates, the roasting must be done under free access

6. Fusion or sintering of ore is likely to retard fu
ization.

7. Sintering does not allow much of the remaining s
the form of sulphate.

Air.—Much oxygen is consumed in roasting sulphid
oxidizing atmosphere is essential to good results. W
fumes, and the products of combustion from the fire-bo
the partly roasted ore in the rear of the furnace, the at
it may not be strongly reducing, is certainly not highl
comparatively small amount of sulphur dioxide in th
will greatly retard oxidation; and if, in addition to sulp
atmosphere is charged with carbon dioxide from the co
fuel, effective roasting is impossible. The only advanta
in passing these deleterious gases over the fresh ore as
into the roasting furnace is to heat it so that oxidation e
rapidly when it reaches a more highly oxidizing atmosph

It is desirable to bring the sulphides to the ignition
soon as possible after the ore has been introduced in
The value of the vitiated hot gasses passing over a long
ore to heat it and thereby save fuel is largely overestim
will exceed the gain.

With a deep bed of ore in the furnace, say from 3 1/
in a highly oxidizing atmosphere, only the ore on the
thorough oxidizing conditions, while that below the su
advantageously placed. If overheated, therefore, fusio
likely to occur in the early stages of the roasting, and
heated too quickly to get a correspondingly quick oxida
occurs, the particles assume a dark, and sometimes glaz
In this condition it is more difficult to sufficiently eliminat
sulphur. The metals, too, are difficult to extract in the c
owing to the inability of the solvent to penetrate the
particles.

Speaking within practical limits, it is not so much th
ture as the lack of air that is fatal to rapid and thoro
reverberatory furnaces. Fusion of the sulphide part
occurs when the ore is brought too suddenly against a hi
with insufficient air. The tendency is to convert th
matte. Much of the sulphur in the deeper portions o
tilizes as such, and when it reaches the surface it burns to
Heat, without access of air, can remove only about 50
sulphur originally in the ore.

The ore in furnace No. 1 was roasted under normal conditions; the bed of ore was about 2 1/2 in. deep; the angle of the rabble blades was 22 1/2 degrees, and the ore was about 2 1/2 hours in passing through. In furnace No. 2 the angle of the rabble blades was changed to 12 degrees, which resulted in having the bed about 4 1/2 in. deep; the ore remained in the furnace about 5 hours to get the same capacity. All the other conditions remained the same, so far as they could be kept the same.

TEST No. 1

	Furnace No. 1 90 tons per day	Furnace No. 2 90 tons per day
Sulphur, raw ore,	2.63 per cent.	2.53 per cent.
Sulphur, roasted ore, soluble,	0.73 per cent.	0.94 per cent.
Sulphur, roasted ore, insoluble,	0.17 per cent.	0.26 per cent.
Sulphur, roasted ore, total,	0.90 per cent.	1.20 per cent.
Assay, roasted ore, gold,	1.07 oz.	2.22 oz.
Assay, chlorination tailings,	0.09 oz.	0.28 oz.
Extraction,	91.5 per cent.	87.4 per cent.

TEST No. 2

	Furnace No. 1 100 tons per day	Furnace No. 2 70 tons per day
Sulphur, raw ore,	2.80 per cent.	2.75 per cent.
Sulphur, roasted ore, soluble,	0.79 per cent.	0.72 per cent.
Sulphur, roasted ore, insoluble,	0.14 per cent.	0.25 per cent.
Sulphur, roasted ore, total,	0.93 per cent.	0.97 per cent.
Assay, roasted ore, gold,	1.80 oz.	1.19 oz.
Assay, chlorination tailings,	0.12 oz.	0.19 oz.
Extraction,	93.3 per cent.	85.3 per cent.

TEST No. 3

	Furnace No. 1 100 tons per day	Furnace No. 2 70 tons per day
Sulphur, raw ore,	2.62 per cent.	2.50 per cent.
Sulphur, roasted ore, soluble,	0.76 per cent.	0.59 per cent.
Sulphur, roasted ore, insoluble,	0.14 per cent.	0.23 per cent.
Sulphur, roasted ore, total,	0.90 per cent.	0.82 per cent.
Assay, roasted ore, gold,	1.90 oz.	1.08 oz.
Assay, chlorination tailings,	0.12 oz.	0.29 oz.
Extraction,	94.0 per cent.	73.0 per cent.

In furnace No. 2 it was soon found that a capacity of 100 tons per day was out of the question. The capacity was at once reduced to 70 tons to give, what at least appeared to be, a fair roast. The bed of ore, which with a capacity of 100 tons was about 5 in. deep, with 70 tons,

It will also be seen from the sulphur analyses that while in test the sulphur is higher in furnace No. 2 than in furnace No. 1, in t and 3, it is lower; nevertheless the extraction was not improved. It noticed, however, that the insoluble sulphur in furnace No. 2 is abnor high as compared with the insoluble sulphur in furnace No. 1. evidently due to lack of air, and perhaps higher temperature, in fu No. 2 to get approximately the same total sulphur elimination as in fu No. 1.

By increasing the bed from 2 or 2 1/2 in. to 4 or 5 in. which the penetration of the air more difficult, the capacity was reduced 100 to 70 tons per day, and the quality of the roast was very in notwithstanding that the time of roasting was practically doubled

The ore in these tests was crushed to 12 mesh, and chlorin hours with a chemical charge of 15 lb. of bleach and 20 lb. of ac ton of ore.

The time of roasting, of 5 hours, in reverberatory furnace may be compared to the time the ore is subjected to roasting in a furnace, which may be considered about half a minute; or 1/600 of the The temperature in both cases may be considered the same; the diff in the results, therefore, is due to the difference in air supply.

Interesting experiments were made in Denver to determine the of an abundance of air supply in roasting charges of 2000 lb. of a hand-rabbled reverberatory furnace. In these experiments, so the charges were roasted in the ordinary way, while in others ar ment was made to pass air through the incandescent roasting ore by up-draft and down-draft; other conditions remained the same. experiments proved that the capacity of the furnace, due to the air supply, was trebled in roasting a heavy sulphide ore; an appre saving of fuel was effected, and the sulphur elimination was more p

The amount of air required in practice in roasting is enormou excess of that required to combine with the sulphur and other ele Theoretically, at least, the air in all parts of the furnace should b as pure as possible; on the other hand, the cost of heating a large v of excess air is considerable. In practice, therefore, the best resul be obtained by carefully balancing these two opposing factors.

The amount of sulphur dioxide in the flue gases for effective ing should not exceed 2 per cent. When the sulphur dioxide furnace atmosphere reaches 4 per cent., roasting becomes slow; it reaches 8 per cent., it becomes very slow; and when it reaches cent. and over, the reactions practically cease.

Rabbling. Rabbling is an important operation in roasting

It is evident that the roasting is facilitated by frequent rabbling but the frequency of the rabbling is limited by the rabbling mechanism in mechanical furnaces, and by the fatigue of the roasterman, in hand rabbled furnaces. Theoretically, the more the ore is rabbled, the better will be the roast, and this theoretical condition should be approached as closely as possible. It is for this reason, more than all others, that mechanical furnaces give a much better roasted product than hand rabbled furnaces. No hand rabbling, on a large scale, can approach the frequency and uniformity of mechanical rabbling.

Effect of Metallic Sulphides if Heated with Exclusion of Air.—Gold and platinum can be completely desulphurized. The sulphide of silver (AgS) remains undecomposed. The sulphides of arsenic, antimony and mercury, volatilize unchanged. Iron pyrites (FeS_2) gives up 23 per cent. of its sulphur, and is reduced to magnetic pyrites (Fe_8S_9), which by a strong heat may be reduced to ferrous sulphide (FeS). The ferrous sulphide is not further reducible. Of the copper minerals, chalcocite (Cu_2S) is not decomposed, but the chalcopyrite ($CuFeS_2$) loses only one part of the sulphur which is combined with the iron. Galena (PbS) is reduced to a lower stage with separation of metallic lead.

Sulphur.—Sulphur usually occurs combined with the base metals as sulphide, but not infrequently the ore is highly charged with sulphates, due to partial decomposition by atmospheric and aqueous agencies. Sulphur, combined with some of the metals as sulphide or sulphate, is highly injurious in the hydrometallurgical process; and if occurring in large quantities, it is fatal. Many of the sulphates are acted upon by acids; in any cases the soluble sulphates affect the leaching solution injuriously. In the cyanide process some of the sulphides, as for example pyrite, are not particularly injurious, while most of the sulphates offer difficulties. In the chlorination process, the sulphur in combination with some of the metals is displaced by the chlorine, which itself unites with the metal or acts as an oxidizer. In either case, the chemicals are consumed by reacting with the base elements, and are not available for action on the desired metals. Roasting, in any event, largely overcomes these difficulties, and in many cases practically eliminates them entirely.

Sulphur is rarely, if ever, entirely eliminated during the roasting. Frequently that which remains is not injurious to the process. The sulphur, as sulphide or sulphate, may be encased in quartz particles, or it may be in the ore as sulphates of the alkali metals or of the alkaline earths. So combined, it is not replacable by any of the chemicals ordinarily used. The sulphates of sodium, potassium, barium, calcium, and

Most of the sulphur in either copper, gold or silver ores is us combined with iron, as iron pyrite (FeS_2). One of these atoms of sul may be distilled, or be burned to sulphur dioxide at a low tempera In the roasting of sulphides, sulphur dioxide is exclusively formed. the presence of air, by catalytic action with indifferent substances as silica or iron oxide, there is always formed a small amount of sul trioxide, which with the moisture of the air and that contained in th and fuel gases, gives sulphuric acid.

The elimination of sulphur from concentrates or heavy sulp ore is accompanied by the evolution of considerable heat. Concent containing from 25 to 35 per cent. sulphur are frequently roasted dov 5 per cent. by the heat generated from their own oxidation. Thirty parts of sulphur, in combining with 32 parts of oxygen (that is, for SO_2), evolves 69,260 heat units; and if the oxidation proceeds to 91,900 heat units are evolved. These figures may be compared with t which correspond to the passage of carbon into carbon monoxide and carbon dioxide (CO_2) when 29,160 and 97,200 units of heat, res tively, are evolved. The evolution of heat by the rapid oxidatio sulphur is practically demonstrated in the various sinter-roas processes in which copper and lead sulphide ore and fines are fused a coherent mass by the heat from the sulphur alone.

The elimination of sulphur, in roasting, varies greatly with diffe ores. Some forms of pyrite are more difficult to roast than ot Unoxidized ores from the deeper levels of a mine are more difficu roast than the partially oxidized ores nearer the surface, even th the sulphur content of both is approximately the same. The chen composition of the ore, aside from its sulphur content, has much t with the roasting. Ferrous sulphate, for example, is much more e broken up than zinc sulphate, or than the sulphates of the alkali alkaline earths. Ore containing much lime is likely to be high in sul after roasting.

In some of the Cripple Creek ores having 2.75 per cent. sulphur best extraction is frequently made, and without undue consumptio chemicals, when the roasted ore contains from 0.60 to 0.80 per sulphur. When the total sulphur in the roasted ore is less than 0.4(cent. the tailing are usually high. Other Cripple Creek ores, whicl partially oxidized, give the best extraction when the sulphur is from to 0.50 per cent., the insolubles usually going from 0.03 to 0.08 per c and the solubles from 0.35 to 0.40 per cent.

It is customary in many of the mills to make frequent sulphur d minations. Sometimes they are made for each shift for every furn

which is soluble in boiling water; usually a little sodium carbonate i added before boiling.

The progress in the elimination of the sulphur, when treating 10 tons of Cripple Creek ore daily in large mechanical furnaces, is show by the following samples taken at various points in the furnace during th roasting. The ore remained in the furnace about 2 3/4 hours, so tha the distance, in feet, from the feed will also closely represent the tim in minutes for the ore in the furnace, when the respective samples wer taken. The ore was rabbled every 17 seconds. The results are average of a large number of sets of samples taken from three different furnaces The samples were taken so as to fairly represent the total cross section o the ore. No. 3 was taken from a type of furnace totally different fro the others. The ore before roasting was crushed to 12 mesh.

No. 3 furnace had a revolving hearth and was fired at a lower tem perature than the others. Notwithstanding the high sulphur conten in the roasted ore from No. 3, the extraction by chlorination was abou the same as for the others. The tailings from No. 2 were somewha higher than from No. 1; this was doubtless due to the fact that in No. 2 with three fire-boxes, the ore had to be roasted at a higher temperatur than in No. 1, which had four fire-boxes.

PROGRESSIVE SULPHUR DETERMINATIONS MADE IN ROASTING CRIPPLE CREEK ORE, IN FURNACES ROASTING 100 TONS OF ORE DAILY

Furnace No. 1 (Four Fire-boxes)

Sample taken, feet (also approximate time in min.) from feed	Distance of fire-box from feed in feet	Sulphur			Difference and difference in per cent.	Per cent of S compared to raw ore	Per cent of S compared to eliminat
		Insol. per cent	Soluble per cent	Total per cent.			
Raw ore		2.60	0.00	2.60			
45 ft. Minutes	55	0.86	0.34	1.20	1.40 ; 76	54	76
65 ft. Minutes	72	0.41	0.49	0.90	0.30 ; 16	65	92
100 ft. Minutes	120	0.23	0.60	0.83	0.07 ; 4	68	96
160 ft. Minutes	140	0.14	0.63	0.77	0.06 ; 4	70	100
Cooler		0.10	0.66	0.76	0.01		

Furnace No. 2 (Three Fire-boxes)

Raw ore		2.58	0.00	2.58			
45 ft. Minutes		1.54	0.19	1.73	0.85 ; 45	33	45

Furnace No. 3 (Revolving Hearth)

Raw ore	2.54	0.00	2.54			
35 min. from feed	1.12	0.29	1.41	1.13 ; 73	44	73
70 min. from feed	0.30	0.80	1.11	0.30 ; 20	56	93
105 min. from feed	0.17	0.93	1.10	0.01 ; 1	56.4	94
165 min. from feed (roasted ore)	0.10	0.90	1.00	0.10 ; 6	60.4	100

In these results it will be noted that much of the sulphur was drive off early in the operation, and before passing the first fire-box. Th is a practical demonstration of the instability of the first atom of sulph in iron pyrite. The difficulty of eliminating the last 25 per cent. apparent; the difficulty of eliminating the third 25 per cent. is considerabl Only a small fraction of the total sulphur is expelled during the last 1(minutes of the 160 minutes of roasting, while a large portion (about on fourth) still remained in the ore. Roasting a low-sulphur ore down to trace is evidently as difficult as to extract all but a trace of the me als. Roasting sulphide ores down to a "trace of sulphur" and extrac ing all but a "trace of the metals" are operations frequently spoken but rarely truthfully realized.

It will be noticed that only from 60 to 70 per cent. of the sulphu was eliminated in these roasts. It is safe to say that fully two-thire of the total fuel was consumed in expelling only a small fraction of per cent. during the latter half of the operation. In the ordinar reverberatory furnace there does not appear to be any adequate gai in the latter part of the roasting, for the fuel expended.

The tables of the progress of roasting give a fair idea as to the rate decrease of the insoluble sulphur and increase of the soluble sulphu After the first 65 or 70 minutes, the principal result accomplished l roasting, is the changing of the remaining insoluble sulphur to th soluble. In furnace No. 3, for example, there is only a difference of 0.1 per cent. in the total sulpur, between the roasted ore and the first 7 minutes of roasting, but for the remaining 85 minutes, 0.30 per cen insoluble sulphur was changed to 0.10 per cent., and this represents th difference between a good and a poor roast.

It sometimes happens that the sulphur in the roasted ore from th cooler is higher than the discharge from the furnace; this may be ac counted for by the fact that the rabbles frequently push more or les partly roasted ore ahead of them in the grooves made by the precedin rabble, or the rabbles themselves may carry partly roasted ore throug the furnace and discharge it on the cooler.

Within certain limits, the sulphur content of the roasted ore does no appear to affect the extraction; beyond these limits the effect is marked Nothing would be gained in extraction by roasting the ore represente in the tables to say 0.05 per cent. insoluble and 0.20 per cent. to 0.40 pe

cent. soluble sulphur, while the extra cost of roasting to such a
phur content would be enormously increased. There would
high tailings from overheating.

There is quite as much danger of over-roasting as under-r
Ore roasted too much will give high tailings, nor can these tai
materially reduced by repeated charges of chemicals. If ore is
roasted, repeated charges of chemicals may be necessary to
desired extraction; but the tailings will be reduced each time, a
mately the limit of extraction may be obtained.

An experiment was made with a 100-ton furnace to determ
effect of ultimate roasting on the extraction. The furnace w
under normal conditions; but instead of treating the ore after
passage through the furnace, it was returned again and again for 1
It is needless to say that the ore was roasted "dead"; neverthel
charges of chemicals on this ore failed to give even the average ext

One of the essential features of roasting is to find the sulphu
minations which will give the best results, and to find the point
lower sulphur content will not appreciably increase the ext
The sulphur in the roasted ore, from one mine or from one distric
has proved to give the best results, might be fatal to the treat
ore from another district. This is largely due to the way in wh
sulphur is combined. Soluble sulphur, as sodium or potassium s
is unaffected by the chemical solvents; if the same amount of
were combined with iron, as ferrous sulphate, the roast would
lutely worthless. Again, the insoluble sulphur, as barium or
sulphate, is not particularly detrimental to the subsequent tre
but if the same amount of sulphur is combined as sulphide, it is alm
to be fatal. Insoluble sulphur does not necessarily imply t
sulphur is in the form of sulphide.

In the roasts, as shown in the accompanying tables, the i
phate was practically eliminated at 100 ft. from the feed, and
eliminated at 120 ft. In some instances it was totally elimi
100 ft., as shown by the ferricyanide test, which did not prod
usual delicate reaction for iron. The ferricyanide test, except for
a rough determination, is absolutely worthless, since it shows
sulphur combined with the iron as soluble sulphate. It fr
happens that the ore is far from being roasted, when the sulphat
is all decomposed.

The barium chloride test, except as a rough indication, is als
less, since it precipitates sulphur that might be considered as p

temperature would be required to break up the sulphates of th earths, and such a temperature would be detrimental to the ex the desired metals.

A direct sulphur determination seems to be the only way of the roast with any degree of accuracy. It is not so much a absolute refinement in the sulphur determination as long as t are uniform. Nevertheless, care and accuracy are essentia formity. The essential idea of the sulphur determination is t the quality of the roast as compared with the extraction. It i material whether the sulphur is relatively high or low. If sulphur determination indicates a good or a bad roast one day, ally at least, it should indicate the same at any other time. It that these ideal conditions cannot always be realized, because ing conditions of the furnace change from time to time. For ore which is over-roasted for four hours on a shift and und the other four, if averaged, might give the same sulphur dete as ore which had been evenly and uniformly roasted for the t hours; but the tailings would be entirely in favor of the la Unless it is known that the conditions of operating the furn changed, it is fair to assume that they have remained the same is usually the case in well conducted plants.

In order to get uniformity in the roasting operation a roasted product, it is essential that the raw ore fed into th should average about the same in sulphur. If the ore co different mines, or from different levels of the same mine, it mixed. Extreme care in mixing is neither necessary nor It is more economical to build the furnace of ample capacit small variations in the ore will naturally be taken care of, unde conditions of operation.

The quantity of sulphur which roasted ore may contain particular detriment is variable, depending largely upon the l nesia, and lead.

Careful tests have demonstrated that an abundance of air i ducive to the formation of sulphates. Air does not appear to sary to decompose sulphates; nevertheless, when it is supplied dance the decomposition of the sulphates is greatly facilitate substances, by catalytic action, may also aid in their decompos

Decomposition Temperature of the Various Sulphates.—Wi ception of lead sulphate, all the common metallic sulphates pletely decomposed upon heating, into metallic oxide, sulphu sulphur dioxide, and oxygen. Some give up their trioxide low temperatures, others require considerable heat and much be completely freed from sulphur. Kerl, in 1881, arranged ciple metallic sulphates, as they are decomposed by a rising

ature, in the following order: silver, iron, copper, zinc, nickel, cobalt manganese, and lead. Lead sulphate is decomposed only at a white heat. Bradford[1] found that ferrous sulphate is decomposed at 590° C. cupric sulphate at 653° C., and silver sulphate at 1095° C. H. O Hofman[2] found that zinc sulphate is decomposed at 739° C.

In the presence of air and other gases, and various other substance in the ore, the temperature of the decomposition of the various metalli sulphates may be vitally affected. The decomposition of silver sulphat takes place at from 860 to 870° C. in the presence of cupric oxide, silica and ferric oxide. In the presence of reducing gases, silver sulphat is decomposed at a very moderate heat, resulting in the formation o metallic silver.

Prof. H. O. Hofman and W. Wanjukow determined the decomposition temperature of some metallic sulphates in a current of air, as follows:

DECOMPOSITION TEMPERATURE OF VARIOUS SULPHATES

Sulphate	Temperature		Product
	Deg. C.	Deg. F.	
$FeSO_4$	150	302	$Fe_2O_3(SO_3)_3$
$Fe_2(SO_4)_3$	530	986	Fe_2O_3
$Bi_2(SO_4)_3$	540	1004	$5Bi_2O_3.4(SO_3)_3$
$CuSO_4$	653	1207	$2CuOSO_3$
$MnSO_4$	680	1256	Mn_3O_4
$2CuO.SO_3$	704	1299	CuO
$NiSO_4$	708	1306	NiO
$CoSO_4$	718	1324	CoO
$ZnSO_4$	739	1362	ZnO
$CdSO_4$	830	1526	$5CdO.SO_3$
$5Bi_2O_3.4(SO_3)_3$	850	1562	Bi_2O_3
$5CdOSO_3$	875	1607	CdO
$CaSO_4$	1200	2192	CaO
$BaSO_4$	1500	2732	BaO

(New York meeting of the American Institute of Mining Engineers, Feb., 1912.)

Amount of Sulphur Trioxide, (SO_3) in the Sulphur Dioxide (SO_2 Escaping from Roasting Furnaces.—In the roasting of Spanish py rites for the manufacture of sulphuric acid it was found that from 2 to per cent. of all the sulphur dioxide was converted into sulphur trioxide

pyrites, containing 48.62 per cent. sulphur, in a glass tube, in a cu of air:

	1	2
Sulphur obtained as SO_2,	88.02 per cent.	88.78 per cent.
Sulphur obtained as SO_3,	5.80 per cent.	6.05 per cent.
Sulphur in residue,	3.42 per cent.	5.17 per cent.
Sulphur lost,	2.75 per cent.	

Of the sulphur of the burner gas there were present:

	1	2
As SO_2,	93.83 per cent.	93.63 per cent.
As SO_3,	6.17 per cent.	6.37 per cent.

Two experiments were made in this way; in the glass tube 50 gr cinders, from the same pyrites, in pieces of the size of a pea, were pletely freed from sulphur by ignition, and fresh pyrites burned as b the gas passing through the cinders. There were found:

	3	4
Sulphur as SO_2,	79.25 per cent.	76.90 per cent.
Sulphur as SO_3,	16.02 per cent.	16.84 per cent.
Sulphur in residue and loss,	4.73 per cent.	6.26 per cent.

Of the sulphur in the burner gas itself there were present:

	3	4
As SO_2,	83.18 per cent.	82.00 per cent.
As SO_3,	16.82 per cent.	18.00 per cent.

Experiments made by Scheurer-Kestner with gases from naces roasting pyrites for the manufacture of sulphuric acid show tha sulphur trioxide is quite variable. One set of determinations made from two samples taken at various times from a lump kiln bu and the other from a Maletra fine ore burner.

The average results of these experiments were:

	Vol. per cent. of SO_2	Sulphur converted into SO_3; per cent. of total sulphur
Lump burner,	7.5 per cent.	3.1 per cent.
Fine ore burner,	8.9 per cent.	3.5 per cent.

The presence of sulphuric acid in the sulphur fumes, espec those from muffle furnaces, is interesting as showing the formati sulphuric acid, probably mostly by catalytic action. This is cl shown in Lunge's experiments Nos. 3 and 4, where the sulphur di was passed through a column of roasted ore, mostly ferric oxide, the amount of sulphur trioxide increased from 6.17 per cent. and per cent. as shown in experiments 1 and 2, to 16.82 per cent. and per cent., as shown in experiments 3 and 4. The amount of sulp acid in the fumes is also interesting from the fact that the acid absorbed in water has been used as the solvent in leaching copper mostly, however, after chloridizing roasting.

Sulphur Determinations.—The following method of making sulphur determinations is used in Cripple Creek mills, where from 30 to 40 analyses are frequently made daily. Instead of determining the soluble and insoluble sulphur from one weighing, two weighings are usually made; one for the total and one for the soluble sulphur. A complete set of samples for one shift consists of an average sample of the raw and roasted ore from each furnace. In this way a check is kept on the work done by the different shifts.

The frequency with which sulphur determinations are made depends upon the uniformity or changeableness of the ore. When ore is roasted for a hydrometallurgical process it is the most important and one of the most delicate steps in the entire treatment, and any indication of the work done by the different shifts is desirable.

Total Sulphur.—Weigh 1.373 grm. of the finely powdered ore into a No. 4 casserole. Add 10 c.c. of a saturated solution of potassium chlorate in nitric acid. Cover with watch glass and boil to dryness. Add 10 c.c. (15 c.c. for concentrates) hydrochloric acid. Evaporate down to about one-half. Add 100 c.c. hot water and boil slightly. Add ammonia until a precipitate of ferric hydrate forms, and then add 10 c.c. of a saturated solution of ammonium carbonate. The ammonium carbonate is to convert any lead sulphate to carbonate and thus render the combined sulphur trioxide soluble as ammonium sulphate. Heat to boiling, remove from the heat, let settle, filter, and wash thoroughly five or six times. Acidulate the filtrate with hydrochloric acid, and then add 5 c.c. in excess. Boil, and while boiling add a hot solution of barium chloride in slight excess. Boil a few minutes longer and let settle. It is best, before filtering, to let the mixture remain hot or boiling slightly, as long as possible, which greatly facilitates the filtering. Filter through a 9 cm. filter, and wash at least six times with boiling water. Ignite, and weigh the barium sulphate.

Since 1.373 grm. were taken, the percentage of sulphur in the ore may be read directly from the scales, 100 milligrm. of barium sulphate being equal to 1 per cent. of sulphur in the ore. In weighing out the 1.373 grm. of ore, instead of making the weighings with the usual gram and milligram weights, a lead button or disc is carefully made so as to weigh 1.373 grm. and this lead button is then always used as the standard weight in making sulphur determinations.

If 1/2 grm. of ore is taken, as may be desirable with ores high in sulphur, the weight of the barium sulphate must be multiplied by 0.1373 to obtain the weight of the sulphur. To ignite the barium sulphate, the filter, with the precipitate, is placed in an annealing cup and

In some of the Cripple Creek mills the step of adding ammonia ammonium carbonate is omitted.

Soluble Sulphur.—Weigh 1.373 grm. of the finely pulverized into a No. 3 casserole. Add about 1/2 grm. sodium carbonate 20 c.c. of water. Boil 5 minutes. Remove and filter; wash thoroughly four or five times with boiling water. Add 10 c.c. hydrochloric to the filtrate, boil, and while boiling add a hot solution of ba chloride in slight excess. Boil a few minutes longer and let s Filter and wash at least six times with boiling water. Ignite by pl the filter and precipitate in an annealing cup and burn in the muffl white. Weigh as for the total sulphur.

Insoluble Sulphur.—The insoluble sulphur is determined by tracting the soluble sulphur from the total sulphur, by taking the weighings from the same carefully mixed sample, and making a so determination on one, and a total determination on the other.

If it is desired to make the two determinations from one weig it is first treated for the soluble sulphur, and then for the insoluble treating it in the same way for the total sulphur.

Tellurium.—Tellurium, the analogue of sulphur, is a common ciate of copper, gold, and silver ores. In recent years it has been f that this element is associated with gold in almost all of the great mi districts of the world, even where not long ago its presence was un pected. It is very common in Cripple Creek, Colorado, in Goldf Nevada, and in the Kalgoorlie mines of Australia. It occurs, the less conspicuously, in the black hills of South Dakota, in the M Morgan mine in Australia, and in the San Juan mines of Colorado. gold in many of the richest mines in the world is associated with t rium and sulphur; the ore is then known as a sulpho-telluride, altho the tellurium is rarely, if ever, found in gold, silver, or copper mi unaccompanied by sulphur. Tellurium also occurs quite univers associated with copper, but in quantities so minute as to be of no sp metallurgical importance. Many of the copper ores of Arizona, Bu Montana, and of Australia contain small quantities of tellurium—ra exceeding two or three hundredth per cent. The matte from the Co Queen, Arizona, contains 0.00088 per cent. tellurium, while that f Butte contains from 0.001 to 0.01 per cent. The anode slimes f electrolytic copper refining, at Butte, contains from 2 to 3 per c tellurium and selenium, and in some electrolytic refineries the sli contain as high as 5 per cent. of these elements.

In the roasting of telluride ores, the tellurium of itself is not of great metallurgical importance. At the most, the quantity of it is usu exceedingly small as compared with the sulphur and other constitue Cripple Creek is widely known as a telluride camp, and yet mill sam rarely show more than a trace of tellurium, and frequently not t

Kalgoorlie is probably the richest tellurium district yet discovered, and yet typical ore analyses show only from 0.03 to 0.10 per cent. of tellurium.

Nevertheless, tellurium is often a source of anxiety to the metallurgist. In sulphide ores the metals, principally gold, are usually fairly evenly distributed through the rock, and the mineral contained in the rock; but not so in telluride ores. By far the greater gold values are intimately associated with the tellurium, so that where a speck of tellurium occurs, there is likely to be associated with it an appreciable quantity of gold also. Tellurium, unlike sulphur, is not usually evenly distributed through the rock. It is ordinarily concentrated within small areas and cleavage planes. The greater portion of the gold in a ton of telluride ore is frequently concentrated in a few rich places. It is this characteristic of telluride ores, as in ores containing free gold in particles of appreciable size, that makes their treatment difficult by a chemical process.

Tellurium fuses at 500° C. (930° F.) and volatilizes at a higher temperature (from 550 to 575° C.). When roasting in an oxidizing atmosphere, it burns with a blue flame edged with green. Sylvanite melts easily tinging the flame greenish-blue. The tellurium combines with oxygen to form tellurium dioxide (TeO_2) which corresponds with the sulphur dioxide (SO_2) formed in roasting sulphides.

The gold compounds of tellurium, usually sylvanite, petzite, and calaverite, all fuse at a low heat, forming at first a globular mass, which, when the tellurium is all volatilized, leaves behind a speck of gold of definite proportions—frequently like a pin head. If the telluride particle is roasted at a low temperature, this speck of gold will be very porous, and present a large surface for attack by the chemical solvent. If roasted at a sudden very high temperature, it is likely to be round and smooth; in this condition the solvents have no appreciable effect on it in the time ordinarily given by a chemical process. When, however, the tellurium is largely associated with sulphur, the sulpho-telluride particle will not fuse, but the sulphur and tellurium will be driven off, as in the case of sulphides, leaving behind the gold disseminated through the ferric oxide particle. If the gold, in roasting, issues from its telluride combination in a shotted form, the best recourse, after the chemical treatment, is concentration. This has proved quite effective. The gold, although usually having a bright yellow appearance, does not amalgamate well. Amalgamation has been tried repeatedly, but has not proved the success that was anticipated; nevertheless, there seems to be no logical reason why it cannot be successfully accomplished.

The difference in the roasting of a grain of sulphide and a grain of

through it in perhaps microscopic particles; in the telluride, o
contrary, unless the utmost care is taken, the grain is likely to fuse i
plastic mass, from which all the gold contained in it will finally e
concentrated into one particle. The solvent, as subsequently a
to the roasted sulphide particle, will extract a very high percent
the gold in a very short time; while the gold resulting from the ro
of the telluride particle would scarcely be affected. Some telluri
are easily treated and show but little coarse gold, but the illust
given shows why it is usual to find coarse gold in the tailings of tel
ores, even when the chemical treatment has been apparently
factory. It is highly probable also that some of the tellurium, by p
fusion, may be converted into a compound which is insoluble, and
resists further oxidation at higher temperatures. This is frequentl
case in the corresponding sulphur combinations, which are insolubl
from which it is difficult to drive off more sulphur by increasing the

Tellurium is insoluble in water and in dilute sulphuric and hyd
loric acids. It is practically unaffected by chlorine, bromine, and
assium cyanide. Gold and tellurium probably form true che
compounds; if this is so, it is evident that the gold cannot be e
extracted unless, in a measure, the tellurium is decomposed. Gol
lurides are very compact and do not permit of much penetration by
solvent. It is largely due to these facts that roasting of telluri
desirable to get low tailings by a solvent process.

There is no appreciable loss of gold by volatilization in the ro
of telluride ores, although at very high temperatures some gold is dou
volatilized with the tellurium. Ordinarily, however, the conditi
roasting are such that the tellurium is volatilized before the temper
is sufficiently high to volatilize any of the gold with it. On comp
the assays of the raw ore with the roasted ore, in mills treating su
telluride ores, no loss by volatilization is apparent with an oxi
roast. Neither does the dust in the dust chambers show a much h
value in gold than the ore from which the dust was obtained. The
difference in value can be accounted for by the fact that the gol
ues in the ore are largely confined to the sulphides and tellurides
owing to their friability a larger proportion of the dust will result
these than from the other constituents. If the gold were appre
volatile with the tellurium, the fumes on cooling in the dust cha
would condense and appear, to some extent, in the furnace dust
there manifest itself in the assays.

Iron.—Iron is inseparably associated with copper, gold and silver
While it is of great importance mineralogically and metallurgica

Ferric oxide (Fe_2O_3), which should be the ultimate condition of the iron in all roasted ore, is insoluble and practically unaffected by all chemical solvents of copper, gold, and silver. It is immaterial whether the solvents are acid or alkaline, or whether they are dilute or somewhat concentrated. If iron gives any serious trouble in roasted ore, it is entirely due to imperfect roasting.

Many raw ores contain considerable quantities of iron as soluble sulphate. This is very pronounced in some mines, and particularly, in the zone of partial oxidation. When this occurs in appreciable quantities, the treatment of the raw ore by any of the chemical processes becomes difficult, and frequently impossible, since all of the chemicals used in solvent processes are quickly affected by it. Washing the ore, either with water or dilute acid or alkaline solutions, is not always effective. Roasting effectively removes the difficulty by converting the ferrous sulphate into the insoluble ferric oxide.

When copper, gold, and silver ores contain simply iron in any of its various combinations with the usual quartz matrix, and without appreciable quantities of any other foreign matter, they can be roasted quickly, thoroughly, and cheaply, no matter what the sulphur content may be, and the values easily recovered with a high percentage of extraction.

Iron, associated with copper, gold, and silver ores usually occurs in the form of:

The Oxide, Hematite (Fe_2O_3), with or without the water of hydration.

The Sulphide, Pyrite (FeS_2).

The Carbonate, Siderite ($FeCO_3$), which, while common, is not general.

When siderite is roasted it is decomposed according to the reaction:

$$FeCO_3 = FeO + CO_2$$

and the molecule of FeO is subsequently converted to Fe_2O_3 by taking oxygen from the air. The roasted carbonate may be strongly magnetic. The temperature must be carefully regulated, to avoid sintering the ore, which because of the fusibility of ferrous oxide and silica, may easily happen. According to Le Chatelier, the decomposition of ferrous carbonate takes place at 800° C. (1472° F.).

The oxidized iron, in copper, gold, and silver veins is usually the result of the natural decomposition of the pyrite by aqueous and atmospheric agencies. With depth in mines, below the influence of these agencies, pyritic ore will be encountered, while at the surface the ore may by perfectly oxidized.

The principle objects to be gained in roasting thoroughly oxidixed ores are dehydration and agglomeration, which much facilitates the sub-

Most of the iron in oxidized ores is in the form of ferric hyd known mineralogically as limonite ($Fe_2O_3+Fe_2(OH)_6$). Ores v consist largely of other substances, such as quartz and clay, us have the characteristic yellow appearance of ferric hydrate. By roas the water of hydration is driven off, which converts the iron int ferric oxide (Fe_2O_3). The color at the same time changes from y or brown to the familiar red of well-roasted ore. In some ore the r very intense.

The ferric hydrate gives off part of its water at a temperature bet 80 and 100° C. (176 and 212° F.) and all of it at a red heat. In heat, in roasting oxidized ores, is not usually necessary, since sulp in appreciable quantities are ordinarily absent. It is the sulp which usually require a higher temperature for their decompos Oxidized ores can be quickly and cheaply roasted; about all that is n sary is to bring the ore to a good red heat.

The magnetic oxide, magnetite (Fe_3O_4), sometimes, though frequently, occurs associated with copper, gold and silver ores. W roasted at a moderate temperature, with an abundance of air, it be converted into the ferric oxide. Roasting with salt appears t much more effective in bringing about this change than a simple oxid roast. Both magnetic oxide and the ferric hydrate dissolve to some ex in acids, and in a smaller degree are converted by chlorine int chloride.

If iron is contained in the raw ore as pyrite (FeS_2), the action of the roasting is to expell one atom of sulphur. This shou accomplished at a moderately low temperature and with an abund of air. The temperature in the early stages of the roasting shoul exceed a dull red. As long, however, as the ore does not show any tend to adhere and form into small lumps there is not much danger of heating. It is well known that one of the atoms of sulphur in pyr quite tenaciously combined with the iron, while the other is held by a feeble bond. In an oxidizing atmosphere at a temperatu about 315° C. (600° F.) the molecule of pyrite beings to be decomp

The sulphur in pyrites, exposed to the direct action of the h heated atmosphere in the furnace, is converted at once into dioxide. the deeper portions of the bed, where it is difficult for the air to p trate, the sulphur may be first volatilized, and on appearing at the face, also burns to sulphur dioxide:

$$FeS_2+O_2=FeS+SO_2$$
$$FeS_2+\text{heat}=FeS+S$$

sulphur trioxide, and the sulphur trioxide combining with the moisture of the air and fuel is converted into sulphuric acid.

The ferrous sulphide, by combining with the oxygen of the air, is converted into ferrous oxide:

$$FeS + O_3 = FeO + SO_2.$$

The ferrous oxide, by combining with more oxygen, may be converted into the magnetic oxide, or by combining with the sulphur trioxide, may be converted into ferrous sulphate:

$$3FeO + O = Fe_3O_4$$
$$FeO + SO_3 = FeSO_4.$$

The magnetic oxide, by proper heating or by combining with sulphur trioxide may be converted into ferric oxide:

$$2Fe_3O_4 + O = 3Fe_2O_3$$
$$2Fe_3O_4 + SO_3 = 3Fe_2O_3 + SO_2$$

The ferrous sulphate, at a red heat, is decomposed into sulphur dioxide, ferric oxide, and ferric sulphate, which on further heating is ultimately decomposed into ferric oxide and sulphur trioxide:

$$6FeSO_4 = Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2$$
$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

The ultimate result of all the reactions is:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

It is desirable to convert all of the iron into the ferric oxide. If the heat is properly adjusted, and the ore remains in a highly oxidizing atmosphere for a prolonged time, the final result will be the ferric oxide. If the heat has been too high or if there has been insufficient air in the furnace, large quantities of magnetic oxide will be formed and remain unchanged. The presence of magnetic oxide in the roasted ore in considerable quantities indicates an inferior roast. Whether it is due to the presence of the magnetic oxide itself, or the condition which produced it, or both is difficult to determine. It has been said that the injurious effects of magnetic oxide is due to its inability to resist the action of the chemicals as well as the ferric oxide; however, in the chlorination and acid processes the consumption of acid or chlorine is less when there is considerable magnetic oxide in the well-roasted ore, nevertheless the tailings are invariably high. The presence of magnetic oxide usually indicates a high tempera-

dark appearace, high tailings may be expected. The extraction is alv the best when the roasted ore has the red appearance of ferric ox The reaction:

$$2Fe_3O_4 + O = 3Fe_2O_3$$

by which the magnetic oxide is converted into the ferric oxide, is rev able:

$$3Fe_2O_3 + \text{heat} = 2Fe_3O_4 + O$$

so that if the heat is too high (about 1700 to 1800° F.), one atom of oxy of the ferric oxide is driven off, and the ferric oxide is converted into magnetic oxide. This is more likely to happen if the atmosphere in furnace is not highly oxidizing, or if the bed of ore is too deep for the to penetrate, or if the ore is insufficiently rabbled.

Magnetic oxide is probably formed in considerable quantities in earlier stages of roasting. The color of many ores, especially th having considerable sulphur, is quite dark while the greater portio the sulphur is being eliminated. It is well known that sulphur dio is a highly reducing agent. The heated top layer of the incandes ore, as it is turned over by the rabble, is ploughed under, so that ferric oxide particles are surrounded by the highly heated reducing atm phere of sulphur dioxide, which results in reducing the ferric to magnetic oxide. The reaction is probably represented by the equati

$$FeS_2 + O_2 = FeS + SO_2$$
$$FeS + 10Fe_2O_3 = 7Fe_3O_4 + SO_2$$

so that this action, and the corresponding reversible reaction by wh the magnetic oxide is reconverted back to the ferric oxide, is likely continue until the sulphur is pretty well eliminated.

The greater part of the iron sulphide becomes sulphate for onl very brief period, especially in the early stages of the roasting. I probable also that sulphate is not formed to any very great extent in ordinary roast. Sulphur determinations taken every hour in roas sulphide ores show very little soluble sulphur in the early stages of roasting, and at any time only small quantities of ferrous sulph Ferrous sulphate is decomposed at about 950° F. (510° C.)

Ferrous sulphate in roasted ore is highly injurious, and shows a v defective roast. It is not difficult to eliminate, but it does not fol that when the ferous sulphate has all been decomposed that the or sufficiently roasted.

There are two substances which offer simple chemical tests for i in solution—potassium ferricyanide ($FeK_3C_6N_6$) and potassium thioc

The test may be made by filtering a sample of the ore with water, then taking a drop of the liquid on paper or on a porcelain plate, and adding a drop or two of the ferricyanide. A blue color indicates the presence of ferrous iron. If the iron is likely to be in the ferric condition, as in the solutions issuing from the ore by the acid or chlorination processes, it should be reduced from the ferric to the ferrous condition before applying the test. Ferric salts are easily reduced to ferrous salts by applying such reducing agents as zinc, stanous chloride, sulphur dioxide, or hydrogen sulphide.

The thiocyanate does not give any marked coloration with ferrous iron, but with *ferric* iron in the most dilute state it forms a bright red soluble compound. The test is made as with the ferricyanide. If the iron is likely to be in the ferrous condition, it should be tested with the ferricyanide, or the ferrous salt converted to the ferric salt before applying the test with thiocyanate.

If no color appears, either with the ferricyanide or thiocyanate, it indicates a thorough roast only in so far as the soluble sulphur compounds of iron are concerned, but not as to the other constituents of the ore. As a final indication of the roast, except perhaps in pure pyritic concentrates, or iron accompanied only by silica, these tests are worthless.

Leaching, or boiling, a little of the roasted ore with water and precipitating with ammonia will usually indicate the soluble iron.

If the ore is so poorly roasted as to show undecomposed sulphides, the roast is worthless. The best way to ascertain if there is any undecomposed sulphides in the roasted ore is to pan it.

Copper.—The mineralogical combinations of copper are quite varied, frequently in the same mine. It may occur as the oxide, carbonate, silicate, or sulphide. The sulphide is by far the most common.

In a typical copper mine, the limonite gossan, usually stained more or less with copper, appears at the surface; below the gossan, in the oxidized zone, are the oxides, carbonates, and silicates; then comes the zone of secondary sulphides consisting of chalcocite, bornite, and chalcopyrite; and below this the primary zone, consisting largely of pyrite interspersed with chalcopyrite.

As the oxide, copper occurs as:

Cuprite, Cu_2O
Tenorite, CuO.

As the carbonate, it usually occurs as:

Malachite, $2CuO, CO_2, H_2O$

As the sulphide, it usually occurs as:

Chalcocite, Cu_2S
Chalcopyrite, $CuFeS_2$
Bornite, Cu_3FeS_3
Enargite, Cu_3AsS_4
Tetrahedrite,

in which the copper occurs as Cu_2S, associated with antimony sulphides, and frequently with iron, lead, zinc, and silver sulp

The carbonates, malachite and azurite, when roasted at are converted into cupric oxide (black oxide), while the carb and water of hydration are driven off:

$$CuCO_3,\ Cu(OH)_2 + \text{heat} = 2CuO + CO_2 + H_2O.$$

The silicate is also converted at a low red temperature to the color changing from the characteristic greenish-blue of to black.

Of the sulphides of copper only the cuprous sulphide (Cu_2S metallurgical importance. Cupric sulphide (CuS) is not stab temperatures, but is decomposed on heating into cuprous su sulphur dioxide. When cuprous sulphide is roasted, the cop converted into cuprous oxide and sulphur dioxide:

$$Cu_2S + O_3 = Cu_2O + SO_2$$

and by contact action is further oxidized into cupric oxide a trioxide:

$$Cu_2O + SO_2 + O_2 = 2CuO + SO_3.$$

Some of the sulphur trioxide, combining with cupric oxide, fo sulphate:

$$CuO + SO_3 = CuSO_4.$$

At a higher temperature, 653° C., the cupric sulphate undergo position, sulphur trioxide being more or less expelled, so that the sulphate will be reconverted into the oxide.

If chalcopyrite, with a quartz matrix, is roasted at a low following reactions take place:

$$3CuFeS_2 + \text{Heat} + O_{18} = Cu_2S + 3FeSO_4 + CuSO_4 + SO_2$$

At 590° C. the ferrous sulphate decomposes, and acting cuprous sulphide remaining, converts it into the cupric sulph

$$Cu_2S + FeSO_4 + O_6 = 2CuSO_4 + Fe_2O_3.$$

At 650° C. the copper sulphate is decomposed into basi and sulphur trioxide, and at 700° C., into cupric oxide an trioxide as follows:

$$2CuSO_4 = CuO, CuSO_4 + SO_3$$
$$CuO, CuSO_4 = 2CuO + SO_3.$$

The ultimate condition of the roasted product, therefore, when carri to above 700° C. are ferric oxide, and cupric oxide. If the temperatu is not carried above 700°, sulphate of copper may remain, while if t temperature is not carried above the decomposition point of fer sulphate, both copper and iron sulphates will remain in the roasted o For a sulphatizing roast, the temperature should not exceed 650° C.

Cuprous sulphide fuses readily, and if contained in the ore in a considerable quantity, must be heated carefully to avoid fusing.

As long as sulphur dioxide is being produced by the oxidation of t sulphur, cupric oxide (CuO) cannot be formed. As soon as all the s phide is converted into a mixture of cuprous oxide and sulphate, t cuprous oxide begins to be converted into the cupric oxide; and if t roasting is continued long enough, all the copper in the ore will be co verted into the cupric oxide, with the probable formation of silicat also, if there is silica present.

With a low temperature, the copper may be contained in the roast ore as cupric oxide (CuO), cuprous oxide (Cu_2O), and cupric sulpha ($CuSO_4$), and this is usually the best condition for copper extractio provided there are no deleterious sulphates in the roasted ore, or undeco posed sulphides. If the ore is poorly roasted, some of the sulphides m remain undecomposed, and this would unfit it for a solvent process. undecomposed sulphides are suspected, it is best to pan some of t roasted material, when the sulphides will be made apparent.

If the amount of copper in the ore is small, as for example in cu riferous gold and silver ores, all the copper sulphide will be convert into the cupric oxide when roasting sufficiently low in sulphur to ma the ore suitable for a solvent process, provided the finishing heat h not been excessive. Whatever the condition of the copper in the r ore, in the roasted ore it will appear as cupric oxide if the ore has be properly roasted.

If the ore is to be treated principally for its copper content, it w not ordinarily be necessary nor desirable to roast to such a comple state of oxidation as in ore treated principally for the precious meta For the acid processes, sulphate of copper is not harmful, and is usual highly beneficial, but no sulphides should be in evidence. If the sa ore is to be treated for gold or silver by the chlorination process t preliminary acid treatment for the extraction of the copper puts it the best possible condition for the extraction of the gold and silver. cyanidation is to follow the acid treatment, a thorough alkaline wash necessary.

The greatest danger in roasting copper ores is in the early stages

ture is excessive during the roasting, ferrites (CuO,Fe_2O_3) and silica are likely to form, and the copper in these combinations is soluble or with the greatest difficulty. It will usually be more satisfactory slightly under-roast copper ore than to take chances in getting the b possible roast by overheating. Copper ores are particularly sensiti to high temperatures, that is to say, temperatures above a dull red (67 C. or 1202° F.) and if sintering or fusion occurs it is practically impo sible to get a satisfactory extraction. Cupric oxide is reduced to c prous oxide at 1050° C.

The best way to determine the best conditions of roasting, pr cipally as to the temperature, is by direct experimenting, and leachi the roasted ore with dilute hydrochloric or sulphuric acid. If t roasting has been properly done, there should be no difficulty in extra ing at least 90 per cent. of the copper. If, however, the temperatu has been excessive, a very poor extraction of the copper may be expecte In making preliminary tests, it is well to roast at least one lot of ore a temperature no higher than scarcely a visible red, and then increase t temperature on successive charges. The percentage of copper extract in a certain reasonable time from the different roasted samples w by comparison, give the highest temperature the ore will stand witho detriment, and that is the temperature at which the ore should roasted.

Whether or not there is any copper sulphate in the roasted ore c easily be ascertained by placing a small portion in a funnel, leaching with hot water, and then adding ammonia to the filtrate, when, if the is any soluble copper, the familiar blue will appear. If no blue appea it may be assumed that the copper in the roasted ore is all in the conditi of oxide.

In gold and silver ores, where the copper does not occur in sufficie quantities to attempt to recover it at a profit, the principal injurio effect of the copper is in the consumption of chemicals, and in its pr cipitation with the precious metals. It is also undesirable in the go and silver bullion, unless there is sufficient copper to make electrolyt refining possible. The extent to which copper in the ores of the precio metals is fatal will depend largely on the price of the chemicals, on t consumption of chemicals, and, in a measure, on the roast. The be ultimate condition of the copper in roasted ore of the precious metals in the form of oxide, and, fortunately, this is the way it usually occu

If the ore is roasted with salt, much of the copper will be convert into cupric chloride ($CuCl_2$), but since at a red heat cupric chloride giv

chloridizing roasting of copper ores is taken up more fully under "Chloridizing Roasting."—"Longmaid-Henderson Process."

The ideal roast for copper ores is one in which all the copper is in the form of sulphate and oxide, and all the iron in the ferric condition. This represents a roast in which practically all the copper is soluble in water or dilute acids, and all the iron insoluble. Since ferrous sulphate is decomposed at 590° C., and cupric sulphate at 650° C., the best roast for the copper, theoretically at least, should be obtained by maintaining the temperature between 590 and 650° C. This also represents the best conditions in practice.

The temperature at which ferrites and silicates of copper are formed has not been definitely determined, but if the ore is heated much above 700° C., there is great danger, and the ferrites and silicates once formed the satisfactory extraction of the copper presents a problem of some magnitude. The presence of ferrites and silicates is usually indicated by the dark appearance of the ore, instead of the red color of ferric oxide.

The sulphur elimination in roasting copper ores depends largely on the amount of copper in the ore, as well as on the amount of sulphur. If much of the copper in the roasted ore is soluble, it is soluble as the sulphate, and the soluble sulphur will be quite large. In this respect roasting of copper ores differs somewhat from roasting gold and silver ores, where the sulphur content of the roasted ore is necessarily quite low. It is not desirable to eliminate the same amount of sulphur from copper ores as from gold and silver ores, so that the roasting of copper ores suitable for hydrometallurgical extraction will usually be somewhat cheaper than if the same ore were roasted for the extraction of the precious metals. On the other hand, copper ores usually require a more delicate roast than gold and silver ores.

For high grade cupriferous concentrates or sulphide ore, the roasted product may contain from 3 to 5 per cent. sulphur, and be well roasted for chemical treatment.

It is possible to make most of the copper soluble by prolonged roasting at a low temperature and with insufficient air, but such a roast will also leave much of the iron and other constituents soluble. Whether this is desirable or not depends almost entirely on the method of precipitating the copper, and on the chemical composition of the soluble iron.

In cases where gold and silver ores contain copper, the roasting must be effected to get the best extraction of those metals, but if a little care is used in the temperature of the roasting, a high extraction of the copper may also be made, even if the ore is roasted with a view of getting the best extraction of the gold and silver.

In order to determine the effect of roasting on chalcopyrite several pounds of the pure mineral, containing as a matrix pure and some galena, was carefully roasted in an assay muffle. T was never above a dull red. The copper content of the raw ore per cent., and the sulphur 28.4 per cent. The sulphur in the roa was 5.5 per cent., of which 3.5 per cent., was soluble. The high i was probably largely due to the galena, forming lead sulphate.

The extraction, by agitating with a 5 per cent. sulution of s acid, was as follows:

Raw ore,	29.3 per cent. Cu.	
Roasted ore, 1 hour's treatment,	3.2 per cent. Cu.	Extraction, 89.1
2 hours' treatment,	2.2 per cent. Cu.	Extraction, 92.5
4 hours' treatment,	1.2 per cent. Cu.	Extraction, 95.9

On the other hand, in just as carefully roasting a sulphide trate from Mexico, containing 6 per cent. copper, it was difficul an extraction of 80 per cent. The mineralogical combination copper in these concentrates was not determined, but presumabl in the form of chalcopyrite or bornite.

Silver.—Silver is universally associated with copper and g may be said that gold in ores is never found unaccompanied b while copper is a common associate of both gold and silver.

Silver is an important factor in the treatment of copper a ores. The silver is not readily recovered, and if contained in the in any considerable quantity, may act as an obstacle to the close tion of the gold. the fact that silver is not readily soluble in an ordinary solvents of copper and gold adds somewhat to the diffi its extraction by the wet processes. Roasting, in the metall silver, is a very important factor.

If there is any free gold in the ore, the silver will be more alloyed with the gold. In thoroughly oxidized ores it probabl in this way. In unoxidized ores it will almost always be foun sulphide, associated more or less with arsenic, antimony, and co will be noticed from the common minerals of silver:

Argentite (silver glance),	Ag_2S.
Pyrargyrite (ruby silver),	$3Ag_2S,Sb_2S_3$
Proustite,	$2Ag_2S,As_2S_3$
Stephanite,	$5Ag_2S,Sb_2S_3$
Stromeyerite,	Ag_2S,Cu_2S
Polybasite,	$9(Ag_2S,Cu_2S),Sb_2S_3,As_2S_3$
Cerargyrite (horn silver),	$AgCl$
Hessite,	Ag_2Te
Petzite,	$(Ag,Au)_2Te$.

While silver is more or less associated with tellurium, it is a strange fact that only a comparatively small quantity of silver is found associated with gold in telluride or sulpho-telluride ores, and is not of any great consequence either in the oxidizing roasting or subsequent chemical treatment. When it does occur combined with gold and tellurium, the tellurium is volatilized in roasting, leaving behind an alloy of gold and silver.

In the oxidizing roasting of sulphide copper and gold ores containing silver, the silver sulphide is first converted into the sulphate at an early stage of the operation. The silver sulphide reacting with the sulphur trioxide, formed principally from iron and copper sulphides by catalytic action with hot silica and metal oxides, forms silver sulphate, and reduces the sulphur trioxide to the dioxide:

$$2Ag_2S + 4SO_3 = Ag_2SO_4 + 4SO_2.$$

If there is any free gold in the sulphide ore, as there frequently is in small quantities, some silver will also be free but alloyed with the gold. This silver in the first stages of roasting is likely to be converted into the sulphate:

$$2Ag + 2SO_3 = Ag_2SO_4 + SO_2.$$

As the ore is rabbled against a higher temperature and a more highly oxidizing atmosphere, the silver sulphate is gradually converted into metallic silver. The silver sulphate is partly reduced by the direct action of heat alone:

$$Ag_2SO_4 + \text{Heat} = 2Ag + SO_3 + O$$

but the temperature required for this reaction—1095° C.—is rarely if ever attained in a roasting furnace. In the presence of reducing gases, silver sulphate is decomposed at a very moderate heat, metallic silver being deposited. In the presence of copper oxides, silica, and iron oxides, silver sulphate is decomposed at temperatures from 860 to 870° C.:

$$Ag_2SO_4 + 4Fe_3O_4 = 2Ag + 6Fe_2O_3 + SO_2$$
$$Ag_2SO_4 + Cu_2O = 2Ag + CuSO_4 + CuO.$$

In the roasting of copper, gold, and silver ores suitable for treatment by chemical processes, in a highly oxidizing atmosphere, the silver in the ore will always be found in the metallic condition, alloyed with the gold. It is for this reason that silver plays so important a part in the hydro-metallurgical treatment, if alloyed in appreciable quantities with gold. Unless the extraction of the silver is quite thorough there may enough remain in the tailings to protect, in a measure, the gold from the action of the solvent.

If the sulphide ore is improperly roasted, some of the silver may

remain as sulphate. As such it is readily soluble in water. One hundred parts of water dissolves 0.58 parts of silver sulphate.

It has been conclusively proved that silver is volatilized in oxidizing roasting. It is possible that in many instances the volatilization of silver in oxidizing roasting is due to the presence of small quantities of cerargyrite, or natural silver chloride. The chloride of silver seems to be quite generally distributed in the various silver ores. The chloride volatilizes at a strong red heat, so that if an excessive loss of silver is discovered in oxidizing roasting it is well to examine the ore to ascertain the presence of chlorine.

Since metallic silver is with difficulty soluble by any of the commercial processes for the recovery of copper, gold and silver, chloridizing roasting is frequently resorted to, in order to convert the silver into the more soluble silver chloride. This subject is taken up in detail under the head of "Chloridizing Roasting."

Any chemical process having for its primary object the recovery of copper or gold from its ores must take cognizance of the silver usually associated with them. If the quantity of silver is small there is no difficulty in recovering a fair percentage by either the cyanide or chlorination processes. If the quantity is large, the best average results will be obtained by chloridizing roasting, when the silver may be extracted quite closely by either the hyposulphite, cyanide, or chlorination processes.

Gold.—Gold, of itself, is of no metallurgical importance in the process of oxidizing roasting. It always occurs native or mixed or combined with sulphur or tellurium; but whether mixed or combined, on roasting it emerges as metallic gold, which at all stages of the roasting is unaffected by any temperature or condition of the furnace. If the gold is free and microscopically fine, coarse, flaky, solid, or porous, it will, of itself, remain so. It will appear in the finally roasted ore as it appeared in the raw ore, or after being liberated in the early stages of the operation.

Much has been said about the loss of gold in roasting. Careful investigation has shown that in oxidizing roasting there is none but a mechanical loss, which is subject to the same conditions as the handling of dry ore under any circumstances. If the ore contains silver chloride, which usually has associated with it some gold, a loss of gold may be expected with that of the silver, in oxidizing roasting, but this loss will ordinarily be very small if the temperature is properly regulated, and in no case will it ever be serious.

Lead.—Lead usually occurs as the

Sulphide (PbS), Galena,
Carbonate ($PbCO_3$), Cerussite,
Sulphate ($PbSO_4$), Anglesite,

Lead is more or less associated with copper and gold ores, but not usually in large quantities. Silver is more commonly associated with it. The presence of lead in ores in small amounts is not particularly harmful, either in roasting or in the subsequent treatment by the hydrometallurgical processes. When lead occurs in ores in large quantities, it is so desirable as a smelting material that its treatment by solvent process is quite remote.

According to Plattner, if the sulphide, galena, is roasted at a low temperature, to prevent fusion, it will at first be converted into the oxide and sulphur dioxide:

$$PbS + O_3 = PbO + SO_2.$$

A part of the sulphur dioxide on coming in contact with the heated silica combines with the oxygen of the air to form sulphur trioxide, and this combines with the lead oxide to form lead sulphate:

$$PbO + SO_3 = PbSO_4.$$

The lead in the roasted ore will usually be in the form of oxide and sulphate. Silicate will not occur unless the ore has been fused, in which case, in any event, the ore would probably be unfit for subsequent chemical treatment. The proportion of the oxide to the sulphate will depend upon the presence of other sulphides, the method of roasting, and to a large extent on the proportion of the galena to the other constituents in the ore.

It is probable that much of the sulphide may be converted directly into the oxide and sulphate by the slow roasting and at the low temperature usually employed in roasting copper, silver, and gold ores for subsequent chemical treatment:

$$2PbS + O_7 = PbSO_4 + PbO + SO_2.$$

When the ore contains considerable lime, as sometimes happens, some metallic lead may possibly be formed:

$$4PbS + 4CaO = 3CaS + CaSO_4 + 4Pb.$$
$$CaS + O_4 = CaSO_4.$$

The transformation of the calcium oxide to the calcium sulphate is a desirable change for the subsequent chemical treatment. Quartz, clay, and silicates remain inert to lead sulphide.

Galena is difficult to roast. It fuses at a low temperature, and if excessively heated, is likely to agglomerate into a mixture of lead oxide and lead sulphate from which it is difficult to expel the sulphur trioxide, even when heated so high as to melt, and from which it is absolutely impossible to satisfactorily extract the copper and precious metals. Lead sulphate, with heat alone, is decomposed only at a white heat.

Lead carbonate ($PbCO_3$) is readily decomposed at a low tem
(200° C.; 392° F.) into lead oxide and carbon dioxide:

$$PbCO_3 = PbO + CO_2.$$

By prolonged roasting, lead carbonate, or the monoxide, at a
ature of not exceeding 450° C. (842° F.) may be converted into t
oxide, minium (Pb_3O_4). At a still higher temperature the
or minium again gives up its oxygen and is reconverted into the
or litharge.

The lead in roasted ore, on cooling, is likely to be in the form
oxide (PbO); rarely perhaps as the red oxide (Pb_3O_4); some
($PbSO_4$), and, if the ore is fused, as silicate.

Ore containing as high as 10 per cent. lead, can with care,
factorily roasted for subsequent chemical treatment.

Zinc.—Zinc frequently occurs associated with copper, g
silver ores as:

Sulphide (ZnS), Sphalerite.
Oxide (ZnO), Zincite.
Carbonate ($ZnCO_3$), Smithsonite.
Silicate (Zn_2SiO_4), Willemite.

In the oxidized ores the zinc usually occurs as the oxide or ca
in the sulphide ores it is always found as sphalerite.

If the zinc is in the form of carbonate, roasting readily drive
carbon dioxide, leaving the oxide of zinc;

$$ZnCO_3 = ZnO + CO_2.$$

If the zinc is in the form of sulphide, oxidation at the tempe
which copper, gold, and silver ores are usually roasted, tak
slowly, and yields a mixture of oxide and sulphate. The am
sulphate, however, is small as compared with the oxide.

Zinc sulphide begins to oxidize at a dull red heat. As the tem
is increased the oxidation takes place more rapidly, with the fo
of zinc oxide and sulphur trioxide:

$$ZnS + O_3 = ZnO + SO_2.$$
$$2ZnS + O_7 = ZnO + ZnSO_4 + SO_2.$$

At a prolonged high temperature the sulphate is converted
oxide:

$$ZnSO_4 + \text{heat} = ZnO + SO_3.$$

In the decomposition of the neutral sulphate, basic sulphates may b formed which require a high and prolonged temperature to ultimatel resolve them into the oxide. Zinc sulphate, by heat alone, is decompose at 739° C.

Zinc sulphide does not oxidize as readily as iron or copper sulphides and a higher temperature is required to start oxidation. It is infusibl at any temperature attained in the roasting furnace, in roasting copper gold and silver ores. Its presence, so far as roasting is concerned, is no harmful.

The relative proportion of zinc oxide and zinc sulphate formed i roasting will depend upon the temperature, the oxidizing qualities of th atmosphere, and, a certain extent, the relative quantity of zinc in the ore The higher the temperature in a highly oxidizing atmosphere, the mor zinc oxide, and the less zinc sulphate, will be formed.

Zinc, though quite generally distributed, is not frequently found i copper, gold, and silver ores in sufficient quantity to interfere with th metallurgical treatment by wet methods. If contained only in smal amounts, and the ore is thoroughly roasted, practically all the zinc wi be in the form of oxide. The oxide is readily soluble in acids, but i not so readily acted upon by chlorine, cyanide or sodium hyposulphite although it affects these solvents injuriously.

Zinc oxide is not volatile at the highest temperature used in roastin ores—from 900 to 970° C. (1652 to 1778° F.). Zinc in its metallic con dition is quite volatile, even at a moderately low temperature. Reducin gases, such as carbon monoxide from the fuel, have a tendency to re duce the oxide to the metallic zinc and thus volatilize it:

$$ZnO + CO = Zn + CO_2.$$

RESULTS OF HEATING ZINC SULPHATE WITH AND WITHOUT FREE ACCESS OF AIR

(H. O. Hofman, Trans. A. I. M. E., 1905)

Heated in	Temp. deg. C.	Total S. eliminated	S. eliminated as SO_2	S. eliminated as SO_3	Ratio: S as SO_2 / S as SO_3
Air.....	578	1.63 per cent	0.14 per cent.	1.49 per cent.	9.06
Air.....	588	1.79 per cent.	0.14 per cent.	1.65 per cent.	8.26
Carbon dioxide.	599	0.50 per cent.	0.18 per cent.	0.32 per cent.	55.25
Carbond dioxide	602	0.50 per cent.	0.16 per cent.	0.34 per cent.	47.88

In these experiments, the temperature of the furnace was brough

show that in heavy zinc sulphate the tendency of the salt to split
ZnO, SO_2, and O is greater when oxygen is absent than when it has
access of air.

Arsenic.—Arsenic usually occurs associated with copper, gold,
silver ores as the sulphide:

Arsenopyrite	(FeAsS), Mispickel.
Realgar	(As_2S_2)
Orpiment	(As_2S_3)

Arsenic is almost universally associated with sulphide copper
If occurring in small quantities it is of no special importance in
roasting except that its elimination should be as complete as pos
under the conditions of the roast. Its presence in the precipitated co
is very harmful, and hence effort should be made to keep the solutio
free from it as possible.

The sulphides of arsenic fuse readily so that care must be exer
in the first stages of the roasting. Arsenic volatilizes at a comparati
low temperature, in the condition of arsenous oxide. In the presen
an excess of oxygen there is a tendency to form arsenates of iron and o
metals, and these arsenates are decomposed only at an exceedingly
temperature. After the arsenic is driven off in the first stages of
roasting, no harm can result in elevating the temperature to tha
quired for the other constituents of the ore. Arsenates are undesi
in the roasted ore, as they interfere with the close extraction of the co
and precious metals. Arsenic in the ore, as a rule, is not particul
detrimental to any of the solvent processes, if the roasting is prop
done.

Mr. R. R. Rothwell, in speaking of roasting arsenical pyrite
Deloros, Canada[1] says, "It was asserted by some metallurgists that
roasting of arsenical pyrites presents many difficulties. I can affirm
the contrary, that they roast with much greater facility and in a
two-thirds of the time necessary to roast simple sulphides. They st
almost any amount of heat without fusing, and the arsenic, which fo
about 49 per cent. of the mispickel, volatilizes at comparatively
temperature, seems to leave the mass porous, thus facilitating the ox
tion of the sulphur." An extraction of 95 per cent. of the gold was m
on these arsenical pyrites by the chlorination process.

At Murcur, Utah, where the ore has been treated successfully
many years by the cyanide process, roasting has been found to elimi
any injurious effects from the arsenic, which occurs in consider
quantities in the raw ore.

the sulphur and arsenic are converted into arsenous oxide and s dioxide. The former is a solid at ordinary temperatures, and the gaseous, and therefore the arsenous oxide is deposited as a sublin the cooler portions of the flues and dust chambers, through whi fumes escape from the furnace.

In roasting cupriferous pyritic ores there will usually be no dif in eliminating from 75 to 80 per cent. of the arsenic.

Roasting Argentiferous Cobalt-nickel Arsenides[1].—The ore used investigation was chiefly smaltite, containing 689 oz. silver per to 56 per cent. arsenic. The object of the investigation was to as (1) the temperature at which the arsenic is most rapidly expell the thoroughness with which it is expelled by prolonged roasting temperature, and (3) the effect of adding charcoal near the end or beginning of the roast.

It was found that 15 per cent. of arsenic per 100 of ore, that is, cent. of the total arsenic, is expelled below 700° C., but that the rest arsenic is not expelled until the temperature reaches about 840° C rapid expulsion sets in. By rabbling at temperatures above 840° percentage of arsenic can be further reduced by about 34 per cent is down to 17 per cent. in the ore, from the original 56 per cent; range of temperature the arsenic is removed much faster than at temperatures. Raising the temperature quite suddenly to 800° C. d harm as the ore remains porous. The addition of charcoal either beginning or toward the end of the roast failed to increase the exp of arsenic. Finer grinding of the ore, after it had been roasted and re-roasting at about 880° C. showed no further expulsion of a due to fine grinding.

Antimony.—Antimony, like arsenic, usually occurs as the sul It is almost universally in the form of Stibnite (Sb_2S_3) and is freq associated with silver and gold, and quite commonly with copper. small quantities in which it usually occurs in the ores of these me does not present any special difficulties in roasting. Care must b in the early stages of the operation. If an attempt were made to r the antimony by rapid oxidation, there would be danger of conv it into the insoluble antimonates of the metals in the ore. This wo undesirable for some of the chemical processes, while for others it be somewhat serious. In the early stages of the roasting it is the necessary to employ a very low heat. The presence of steam, supplied by the burning fuel and the water of hydration in the found to be useful as a source of hydrogen, which removes sulp hydrogen sulphide:

$$Sb_2S_3 + 3H_2 + \text{heat} = 3H_2S + Sb.$$

[1] *Bi-Monthly Bulletin* of the A. I. M. E., Jan. 1907.

The antimony then combines with oxygen and escapes as a v oxide.

When the temperature of the roasted ore is brought to about 3 (662° F.) the atmospheric oxygen converts the antimony trisulphid antimonous oxide and sulphur dioxide. Antimonic acid is formed presence of the oxides of the other metals, and combines with th form antimonates. Sulphates of antimony are not formed durin roasting. If the ore contains large quantities of foreign sulp which on being roasted would form sulphates, antimonates of the f metals are formed instead of the sulphates.

Carbon, such as coal or charcoal, finely ground or mixed with th has been used to break up the antimonates and arsenates, and exp arsenic and antimony, but it has not been found of utility enough t a permanent place in practice.

All ores of copper, gold, and silver, containing appreciable quan of arsenic and antimony, are difficult, if not impracticable, to treat by any of the solvent processes. By roasting, and consequent vo zation of these elements, they are largely eliminated from further c eration, except, perhaps in the case of silver ores to be treated by s hyposulphite, when the ores may contain considerable quantities of ates and antimonates, after roasting.

Antimonous oxide (Sb_2O_3 or Sb_4O_6) resulting from the roasti antimony sulphide (Sb_2S_3) is insoluble in water, but is soluble in h chloric acid and in alkalies.

Bismuth.—Bismuth is one of the most injurious alloys of copper may be present in copper ores in the metallic state, or in sulp arsenides, and antimonides. The metal and sulphides are volatile roasting temperature but much less readily than in the cases of a and antimony. The minerals containing bismuth are readily oxi to fixed compounds.

In the incomplete roasting of copper ores, arsenic, antimony bismuth may remain in the roasted product in the same combin in which they occurred in the ores, accompanying the fixed comp that are formed during the roasting operation.

The degree of elimination of these impurities in roasting necessarily with the minerals in which they occur, as well as the c ore, and the conditions under which the roasting is carried on. following analytical data by Allan Gibb[1] shows the elimination from typical ores, when roasted in heaps and in reverberatory furnace smelting, which does not represent as complete a roast as that req

ROASTING COPPER ORES; ELIMINATION OF ARSENIC, ANTIMONY A
BISMUTH

	Raw ore		Roasted ore		Elimination per 100 of Cu	Total p centage elimina
	Per cent. actual	Per cent. relative Cu=100	Per cent. actual	Per cent. relative Cu=100		
			No. 1			
Copper.....	5.55	100.00	7.68	100.00		
Arsenic.....	1.18	21.36	0.407	5.29	15.97	75.0
Antimony.....	0.035	0.63	0.035	0.47	0.160	25.4
Bismuth.....	0.011	0.198	0.011	0.143	0.055	27.8
			No. 2			
Copper.....	12.15	100.00	14.68	100.00		
Arsenic.....	0.967	7.96	0.454	3.09	4.87	61.2
Antimony.....	0.46	0.378	0.045	0.307	0.071	18.8
Bismuth.....	0.014	0.115	0.015	0.013	0.013	11.3

No. 1 was a cupriferous iron pyrites which was roasted in heaps a subsequently smelted in blast furnaces.

No. 2 was a dressed ore containing the copper mostly in the form copper pyrites, with a small proportion of bornite and copper glan It was roasted in a reverberatory furnace.

Nickel.—Nickel is quite frequently associated with copper ores, a when it so occurs in paying quantities its recovery is advisable.

Nickel usually occurs as the
Sulphide, Millerite, NiS,
Arsenide, Niccolite, NiAs,
Silicate, Garnierite, H (NiMg)SiO_4, H_2O.

When the sulphide is roasted, the nickel is oxidized and the sulp passes off, mostly as the dioxide, and some as the trioxide. The oxide produces sulphuric acid and forms some nickel sulphate. Wh the sulphate is strongly heated the nickel is converted into nickel oxide and sulphur trioxide is driven off. By prolonged roasting, at proper temperature, nickelous oxide, NiO, alone may be obtained. imperfectly roasted, there will be a mixture of oxide, sulphate, a unaltered sulphide.

If a mixture of nickel and iron sulphides is carefully roasted, a m ture of nickelous oxide and ferric oxide is obtained. As sulphate nickel is a very stable compound, the roasting may be so conduct that the greater part of the nickel is obtained as sulphate, while the i will be in the condition of ferric oxide.

By roasting nickel and copper sulphides in the same way, it to get nickelous oxide and cupric oxide, or a mixture of oxid phates. As nickel sulphate is stable at a higher tempera copper sulphate, the nickel may be roasted to the sulphate and to the oxide.

If nickel, iron, and copper sulphides are all roasted tog nickel may be in the condition of sulphate and the other two ferric and cupric oxides.

If nickel arsenide is roasted, the arsenic forms arsenous the nickel sesquioxide. Part of the arsenous oxide escapes part is further oxidized to arsenic oxide, and this combine nickelous oxide to form an arsenate. Nickel arsenate is not d when heated alone, so the result is basic nickel arsenate.

Copper ores containing nickel usually contain also magnet pyrites, and often arsenic and antimony compounds as well a quartz, and earthy matter. In the roasting, the arsenic and an mostly driven off, the sulphur partly escapes as dioxide, an converted into trioxide by contact with the red-hot masses furnace walls. Iron, copper, and nickel oxides combine with th to form sulphates. As the roasting proceeds, and the temp raised, the sulphates are again decomposed into oxides ar trioxide, or sulphur dioxide and oxygen. Iron sulphate is fi posed, next the copper, and lastly the nickel compound. If th were continued at the proper temperature, the product w mixture of ferric oxide, cupric and cuprous oxides, and nicke

Nickel sulphate is readily and abundantly soluble in w oxide is soluble in mineral acids, especially dilute hydroch when warmed. The chloride is soluble in water, but not as the sulphate. The mineral garnierite is soluble in sulphuric a chloric acids, but with some difficulty.

Calcium (Lime).—The compounds of calcium, on accour prevalence and positive action on almost all of the chemical sol in the hydrometallurgical processes, are among the most impo considered. In the alkali process, calcium compounds are n larly harmful, and frequently, as in the case where calcium is com oxygen to form lime, it imparts a desired alkalinity before ap solvent. In the acid processes, like chlorination or the treatmen ores with dilute acids, the amount of calcium in the ore and th combined will usually be the most important factor in deter applicability of the process and, to a large extent, indicate its failure.

There would be no difficulty in treating most of the coppe silver ores successfully, by the acid processes, if it were not interfering elements, and of all the interfering elements, the p

lime in large quantities presents the most common and the most difficult problem. Fortunately, most of the ores of copper and the precious metals do not contain enough lime to seriously interfere with the treatment. The vast majority of all metalliferous deposits have quartz as the matrix, and usually the lime is not found in quantities sufficient to make an acid treatment prohibitive, if the ore is otherwise suited to the process, particularly if the ore is amenable to preliminary concentration.

Calcium usually occurs associated with copper, gold and silver ores in the form of

The Carbonate ($CaCO_3$), Calcite (Limestone).
The Fluoride (CaF_2), Fluorite.
The Sulphate ($CaSO_4$), Gypsum.

The carbonate is not readily attacked by chlorine, but is immediately decomposed by acids. Roasting converts the carbonate into the oxide and carbon dioxide:

$$CaCO_3 + Heat = CaO + CO_2.$$

When cold, the oxide (lime) does not absorb chlorine, but at a red heat, in the presence of chlorine, it forms calcium chloride with the evolution of oxygen:

$$CaO + 2Cl = CaCl_2 + O.$$

If the ore contains considerable sulphur, the sulphur trioxide released during the roasting combines to a greater or less extent with the lime to form sulphate:

$$CaO + SO_3 = CaSO_4$$

which is practically unaffected by all the acids, only very slightly acted upon by chlorine, and remains neutral to cyanide or sodium hyposulphite. It is almost insoluble in water; one part of calcium sulphate requires 432 parts of water for its solution. Its solubility is increased by the presence of alkaline chlorides and free hydrochloric acid.

It is desirable, therefore, that ores containing considerable lime should be mixed with ores containing considerable sulphur before roasting. Some of the calcium, however, will unavoidably remain as oxide after roasting, which, when coming in contact with water in the subsequent chemical treatment, is converted into the hydroxide (slacked lime) in which form it is desirable in the alkali processes, but is readily attacked by chlorine and the acids.

The lime, when coming in contact with sulphuric acid, as in the sulphuric acid copper processes, and the barrel chlorination process where

which accounts for much of the excess of acid sometimes used in tre ores containing considerable lime.

In order to economize acid, it is desirable to convert as mu possible of the lime into the sulphate, by judicious roasting, if the a sulphide.

If the chlorinating is done by the "Plattner" or by the "Percola processes, in which acids are not ordinarily used, then the lime, ins of combining with the excess of acid, will combine with the chlorine

$$2Ca(OH)_2 + 4Cl = CaCl_2 + Ca(ClO)_2 + 2H_2O,$$

forming the chloride and hypochlorite, as in the manufacture of blea powder. Since chlorine acts more readily on lime than on copper, and silver, in the ore, sufficient chlorine must be provided to chlor the lime and have an excess after all other base elements have satisfied. To avoid the large consumption of chlorine when it is ap directly as gas in ores containing much lime, the ore is frequently ro with salt; in this way the lime is converted into chloride in the furnace is no longer harmful.

Calcium, in the form of fluorite, is a common associate of copper, and silver ores. It occurs abundantly in Cripple Creek, intimately as ated with calcite. Fluorite is peculiarly a constituent of metallif veins. In minute quantities it is widely diffused.

Fluorite is unaffected by chlorine, cyanide, or dilute acids. concentrated sulphuric acid decomposes it. By roasting, the fluori converted into the oxide, as in the case of carbonate:

$$CaF_2 + H_2O = CaO + 2HF.$$

The fluorine probably combines with the moisture of the air, water combined in the ore as hydrate, to form hydrofluoric acid.

Mixed with silica and sulphur, as the fluorite usually is in metall ous ores, the sulphuric acid formed in the roasting converts som the calcium into the sulphate:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
$$CaF_2 + 2H_2SO_4 + SiO_2 = CaSO_4 + 2H_2O + SiF_4.$$

The principal point of interest, so far as roasting for the subseq chemical treatment is concerned, is, like the carbonate, the fluori converted into lime, and that in the presence of sulphur it is conve into the sulphate.

A specimen sample of Cripple Creek ore, composed largely of fluo after roasting had a white appearance, and analysis showed 39.25

result of the decomposition of pyritic ores acting on the calcium carbonate Pyritic ore is oxidized by the action of water and air, forming ferrous sulphate and sulphuric acid.

$$FeS_2 + H_2O + O_7 = FeSO_4 + H_2SO_4.$$

The sulphuric acid then acts on the carbonate, forming calcium sulphate and water:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O.$$

Calcium, therefore, in oxidized ores is largely in the form of sulphate and is not particularly injurious in any of the chemical processes, or in the roasting operation. The sulphate, once formed, can only be converted into the oxide by the most intense heat procurable. Such a heat is never realized in a roasting furnace.

Gypsum gives off its water of hydration at 200 to 250° C. (392 to 482° F.). The dehydrated gypsum melts at a red heat without decomposition. On coming in contact with water, the dehydrated calcium sulphate again takes up its water of hydration, just as in the case of ordinary plaster of Paris. In doing this, if the ore contains considerable sulphate it sometimes happens that the ore during leaching sets so hard that picks have to be used to remove it from the vats.

An analysis made on unoxidized ore from Cripple Creek, showed:

Calcium Sulphate (gypsum, $CaSO_4 + 2H_2O$),	0.83 per cent.
Calcium Fluoride (fluorite, CaF_2),	0.78 per cent.

The amount of lime in an ore which may be fatal to chlorination or to an acid treatment depends largely on other conditions. Ordinarily from 5 to 6 per cent. is the limit. In Cripple Creek ores the lime varies from 1.5 to 2.5 per cent., although in some mines it is much higher. The Potsdam ores of the Black Hills, which have been successfully chlorinated, contain as much as 8 per cent. CaO.

That only a small portion of the lime in roasted ore combines with chlorine or the acids is evident from the treatment of 800 to 1000 tons daily of Cripple Creek ores by the barrel chlorination process, where it may be assumed that the ore averages 2 per cent. lime, or 40 lb. per ton. The average chemical charge may be assumed to be 15 lb. of bleach and 30 lb. of sulphuric acid. Theoretically, it takes 6 parts of acid to combine with 7 parts of bleach, but in practice, owing to the impurities of the bleach and acid, equal parts of each are required. Of the 30 lb. of acid therefore, per ton of ore charged into the barrel, 15 lb. are consumed in reacting with the bleach to generate chlorine. The solutions issuing from the barrels after treatment are always strongly acid, so that much acid remains unconsumed, and some is also consumed in reacting with other base elements. It is safe to say, therefore, that only from 5 to 10 lb

of the acid actually combines with the calcium or lime in the ore. if the calcium in the ore were all present as lime, that is 40 lb. Ca(would take at least 70 lb. of acid to neutralize this lime, instead of 5 or 10 lb. actually required in practice. Some of the Cripple Creek are chlorinated with only 10 lb. of bleach and 15 lb. of acid, which m the acid consumed considerably less. From this it will be seen that injurious effect of the lime in ore in an acid process depends largely o chemical combination, and that much of the lime in sulphide ores be converted into a comparatively harmless condition by roasting.

Magnesium.—Copper, gold and silver ores frequently contain s quantities of magnesium, but usually not in sufficient quantity to ously interfere with any operation in the hydrometallurgical proce For all practical purposes of hydrometallurgy it may be considere equivalent to its analogous element, calcium. Magnesium usually oc combined with calcium as:

The Carbonate, $(CaMg)CO_3$, Dolomite,
The Sulphate, $MgSO_4,H_2O$, Kieserite,
The Silicate, $H_4Mg_3SiO_9$, Serpentine,
The Silicate, $H_2Mg_3(SiO_3)_4$, Talc.

In oxidized ores the magnesium is largely in the form of carbonate silicate. It may also be present as sulphate, formed by the decom tion of pyrites, as the corresponding calcium sulphate. The magne sulphate, kieserite, is very slowly soluble in water—about like gyp The hydrous sulphate epsomite ($MgSO_4,XH_2O$) is readily soluble. roasting, this water of hydration is driven off. Much of the magne sulphate formed in the oxidation of pyrites in mineralized veins is ca away in solution.

In roasting sulphide ores, the magnesium carbonate is partly verted into the oxide and partly into the sulphate. The oxide, lik corresponding calcium oxide, is practically insoluble in water reacts readily with chlorine, bromine, hydrochloric and sulphuric aci form the chloride, bromide, and sulphate. Magnesium chloride is soluble in water—100 parts of water will dissolve about 52 par magnesium chloride at ordinary temperatures.

Magnesium sulphate is practically unaffected by any of the c ical solvents. All the harmful hydrous sulphates may be conv into the harmless anhydrous sulphate by roasting. As in the ca calcium, therefore, ore containing magnesium should be roasted w view of converting as much of it as possible into the form of sulp

Manganese.—Manganese is one of the most deleterious substances in the extraction of metals by wet methods. It affects injuriously the acids, the halogens, and cyanide. Fortunately it does not frequently occur in ores of copper and the precious metals in quantities so great as to be fatal.

Manganese almost universally occurs as the oxide; sometimes as the sulphide and silicate. After roasting it is always in the form of oxide, and roasting does not materially lessen its injurious effects on the solvent. Manganese is readily soluble in acids and difficult to eliminate from the solvent. Its principal injurious effect is in the consumption of chemicals.

Aluminum.—Aluminum, as it occurs in copper, gold, and silver ores, affects the chemical processes somewhat injuriously. Its mineralogical combinations are numerous and varied. It may occur as the oxide, hydroxide, sulphate, or silicate. It usually occurs as the silicate, more or less intimately associated with calcium, magnesium, iron, and the alkali metals.

Roasting converts some of the aluminum compounds into aluminum oxide (Al_2O_3), which is infusible at all temperatures ever attained in a roasting furnace. It is not decomposed by heat alone. It is not decomposed by chlorine at any temperature. Anhydrous aluminum oxide is perfectly insoluble in water. After strong ignition, it is likewise insoluble in most acids. The lower the temperature at which aluminum oxide is heated, the more soluble it is in the acids and alkalis.

All the silicates of aluminum are insoluble in water, with the exception of the alkali salts, and these are soluble only when the ratio of the base to the acid is above a certain limit. Many of the silicates are decomposed by dilute sulphuric and hydrochloric acids. Chlorine, bromine, and potassium cyanide react very slowly.

Aluminum sulphate, $Al_2(SO_4)_3$, when heated to redness, is converted into the oxide. The sulphate is very soluble in water. Chlorine reacts very slowly with it. The basic sulphate, $Al_2O_3, SO_3, 10H_2O$, is insoluble in water, but soluble in sulphuric and hydrochloric acids.

When ores containing considerable aluminum are properly roasted, and a sample filtered with water, it will be found on testing that there is no soluble aluminum in the ore. If the sample is then filtered with dilute sulphuric or hydrochloric acid, some aluminum will be dissolved. If the sample is treated with chlorine, bromine, or potassium cyanide, only traces will be found in the solution.

The compounds of aluminum are so numerous, varied and complicated that it is difficult, if not impossible, to determine their exact composition either in the raw or roasted ore. The only alternative seems

increased cost of treatment, due largely to increased consumption of acid, no great injury to its presence in the ore is apparent. Its presence, even in large quantities, is not fatal, or even serious, to any chemical process. Cripple Creek ores, which are very successfully treated after roasting, by cyanidation, and by chlorination with or without the use of acid, frequently contain as high as 20 per cent. alumina (Al_2O_3), and the average is about 18 per cent. Copper ores at Clefton, Arizona, containing 16 per cent. alumina have been successfully leached for many years with sulphuric acid.

Usually copper, gold, and silver ores do not contain more than several per cent. alumina; frequently it is less than 1 per cent. Whatever the condition of the aluminum in the raw ore, where it may be injurious, the tendency in roasting is to convert it into the harmless aluminum oxide. The higher the temperature at which the ore is roasted, the less difficulty will result due to the presence of aluminum, but the ultimate temperature of roasting ores containing much aluminum will depend on the other, more or less fusible, constituents.

The hydrate of aluminum occurs mineralogically as Gibbsite; it is easily dissolved by acids. The monohydrate occurs native as diaspore; it gives up its water of hydration at 360° C. (680° F.).

Clay.—This is the term applied to hydrous silicates of aluminum, produced for the most part by the decomposition of feldspar rocks, and generally mixed with other substances, chiefly lime, magnesia, and oxide of iron. Clay is frequently a constituent of ores, usually occurring as "Gouge" matter in the vein.

As a rule clays contain from 45 to 60 per cent. silica; from 20 to 30 per cent. alumina; from 0.5 to 3 per cent. lime; from 0.5 to 3 per cent. magnesia, small quantities of iron, and about 10 per cent. water. Clays always contain a hydrous compound of alumina and silica, which is able to give up the alumina contained by it as a base to sulphuric acid.

Clays are very much improved by roasting, both as to filtration and chemical consumption.

Barium frequently occurs associated with copper, gold, and silver ores in small quantities. It is usually in the form of sulphate, Barite (heavy spar, $BaSO_4$). Sometimes it occurs as the carbonate, Witherite ($BaCO_3$).

If the carbonate is heated in an atmosphere free from sulphur, the barium oxide, BaO, will be produced, which reacts with the halogens and the acids. The temperature required for the decomposition of the carbonate by heat alone is very high. In the presence of sulphur, the carbonate is converted into the sulphate.

Barium sulphate is practically unaffected by any operation of the chemical processes. Any heat obtainable in a roasting furnace does not decompose it. It is insoluble in water and in acids.

Alkali Metals.—The alkali metals, sodium, and potassium, are frequently found in considerable quantities associated with ores. They usually occur as the feldspars or hornblende, and as such are unaffected by roasting or any of the chemicals used in the solvent processes.

Chlorine, Bromine.—Chlorine and bromine are sometimes found in copper, gold, and silver ores, and when they do so occur are of considerable metallurgical importance in roasting. The compound which is most common is the silver chloride, cerargyrite (AgCl). The minerals embolite, Ag(ClBr), and bromyrite, AgBr, occur occasionally, and in roasting may be considered the same as cyrargyrite. Chlorine also occurs quite frequently in combination with lead.

The surface ores of Tonapah, Nevada, show much of the silver combined with chlorine—frequently as much as 20 per cent. As depth is attained, the silver chloride gradually merges into the sulphide, although the chlorides appear never to be entirely absent.

The principal point of importance in connection with the roasting of silver chloride, is the danger of volatilization, even with an oxidizing roast. In making exhaustive tests in Denver, on a working scale, on some of the Tonapah ores, it was found that the volatilization, with an oxidizing roast, was about the same as with a chloridizing roast, but in no case was the volatilization serious. If volatilization is known to take place in an oxidizing roast, chlorides in the ore may be suspected.

To ascertain the amount of silver chloride in the ore, leach, or treat a sample with sodium hyposulphite (sodium thiosulphate) and compare the hypo tails with that of the original ore. Also test for chlorine with silver nitrate.

Loss of Weight in Roasting.—There is always some loss of weight in ore due to roasting. The loss is usually largest in pyritic ores and in pyritic concentrates, but it may also be considerable in ores which are oxidized and highly silicious. In sulphide ore the loss is due mostly to the expulsion of the sulphur; in oxidized ores it is mostly due to driving off the water of hydration. The water so combined, in many ores may be quite large. Iron in oxidized unroasted ores is almost always in the form of ferric hydrate (limonite), $2FeO_3$, $3H_2O$, which contains 14.4 per cent. water, all of which is driven off in roasting. Similarly other substances give up their water of hydration, and some of the elements are eliminated by volatilization.

The loss of weight in sulphide ores is represented by the substitution of oxygen for sulphur. From the equation

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

the loss of weight of pyrites can readily be calculated that 3 parts of $FeS_2 = 2$ parts Fe_2O_3, but the matter is usually not so simple as this, owing to other constituents in the ore and the manner in which the remaining

sulphur is combined. If, for example, there is galena (PbS) in the ore and is oxidized to sulphate ($PbSO_4$), there has been an actual gain of weight of 4 atoms of oxygen, or 27 per cent.

The loss of weight can readily be ascertained from the difference in weight between the raw and roasted, as it is charged and withdrawn from the furnace. This method is expensive and not quite accurate because the dust loss cannot usually be taken into consideration. The loss of weight is best and most conveniently obtained by direct experiment. This is done by weighing a small average sample of the ore, then thoroughly drying it; weighing it again, and then roasting it in a roasting dish, in a muffle, to the same extent as the ore is roasted in the mill. A sulphur determination will show this. From the differences in weight between the raw ore, the dried ore, and the roasted ore, the loss due to moisture and the loss due to roasting can easily and accurately be ascertained.

A ton of roasted pyritic concentrates will occupy about 24 1/2 cu. ft. This is derived from 2800 lb. of raw ore, which will occupy about 23 2/3 cu. ft. per ton. A ton of the concentrates after roasting will weigh from 1450 to 1700 lb., and will occupy about 17 1/2 cu. ft. The loss of weight in Cripple Creek ores, due to roasting, is usually from 5 to 7 per cent., based on the control samples. Of this loss, about 2 per cent. is for moisture, and from 3 to 4 per cent. dust and volatilization loss. Of the volatilization loss about 1 per cent. is accounted for by the elimination of the greater portion of the sulphur. The accountable dust loss is about 2 per cent., and the unaccountable loss amounts to about 1 per cent. Much of this unaccountable loss is due to unsettled dust going out of the furnace stacks, and some also due to unrecovered dust in crushing and roasting other than flue dust.

At Butte, in roasting copper concentrates, containing 35 per cent. sulphur down to 7 per cent. sulphur, the loss of weight, including flue dust, is about 20 per cent.

In roasting Black Hills ore, containing 11 per cent. sulphur, down to 0.08 per cent., there was a loss in weight of 21 per cent., even though the ore was apparently thoroughly dry. This ore was very talcy, and the great loss was evidently due principally to the water of hydration.

CHAPTER IV

CHLORIDIZING ROASTING

Object of Chloridizing Roasting.—Most of the chlorides, at elevated temperatures and in the presence of sulphides or sulphates, have the power of converting copper and silver into their respective chlorides, and, to some extent, the gold also. To roast in the presence of chlorides, usually sodium chloride (common salt), is known as "Chloridizing Roasting." The term "chloridizing" is limited to the production of chlorides by the interchanging of chlorine from its chloride combinations, usually at elevated temperatures; while the term "chlorinating" is limited to the production of chlorides, usually in the wet way, by the application of free chlorine.

The objects of chloridizing roasting are:

1. In copper ores, or in gold and silver ores containing copper, to convert the copper into chlorides, which will not react with chlorine or the acids, but which are directly soluble in water or in chloride solutions.

2. In silver ores, or in gold and copper ores containing silver, to convert the insoluble metallic silver or its insoluble compounds, into the more soluble silver chloride.

3. In any ore, to convert the harmful elements into less harmful compounds.

4. To assist in a more efficient oxidizing action than is possible under the same conditions, in ordinary oxidizing roasting.

Metallic silver is not readily soluble in any of the commercial chemical solvents. The silver chloride is readily soluble, either in chloride solutions, sodium or calcium hyposulphite, or in potassium or sodium cyanide. If, therefore, a high percentage of the silver can be converted into the chloride, a quick and correspondingly high percentage of the silver can be extracted.

If the ore contains copper, or if a copper ore is treated by a chloride process, it is frequently desirable to convert the copper in the ore into the soluble cupric chloride, so as to save acid, if an acid process is used. It may be cheaper to convert the copper into chlorides at the expense of a cheap material, such as salt, than to let the oxides react with the more expensive acids. Chloridizing roasting is largely used in the extraction of copper from its ores.

Most of the chlorides are soluble in water; if desired, many of the objectionable elements in the ore may be removed by a preliminary washing, after roasting, and before applying the chemical solvent.

Of the metallic sulphides usually associated with copper, gold and silver ores, those of iron, copper, lead, and zinc are the most common. Of these, only the iron and copper sulphides, are available to react with the salt; while those of lead and zinc remain quite indifferent.

Adaptability of the Various Ores to Chloridizing Roasting.—Ottokar Hofmann[1] aptly classifies the adaptability of the various ores to chloridizing roasting, as follows:

1. Those like iron and copper pyrites, gray copper ore, and silver copper glance, which in roasting form sulphates, and decompose salt, liberating chlorine.

2. Those like galena and zinc blende, which form sulphates remaining indifferent to salt.

3. Antimonial and arsenical silver minerals which form antimonates and arsenates of silver.

The gangue remains indifferent, like quartz or porphyry, or it takes an active part, like limestone, talc, spar, manganese, and minerals containing magnesia.

If ore consists of minerals of the first group together with an indifferent gangue, chloridizing roasting offers no difficulty and a high chloridization can be obtained without much loss of silver by volatilization and no special skill is required in the roasting; neither does it matter if the salt is added to the charge before entering the furnace or after it has been subjected to partial oxidizing roasting.

The process of chloridizing roasting becomes more difficult if one or both of the minerals of the second class are present in large quantities, even if associated with an indifferent gangue. With such ores the time of adding the salt becomes very important. If added before the charge enters the furnace a very inferior chloridization is obtained, as is also the case if the salt is added before the oxidizing period has sufficiently advanced. Moreover, the temperature and air supply require much attention.

The roasting is still more difficult if all the classes of ore are represented in connection with a gangue like limestone which takes an active and injurious part in the operation.

Chemistry of Chloridizing Roasting.—The sulphides in the ore, mostly relied upon for chloridization, are those of iron and copper. The sulphates of these metals, formed during the roasting, react with the salt to form sodium sulphate and the chlorides of the metals. Some hydrochloric acid and chlorine are formed at the same time, largely due

[1] Mineral Industry, 1896.

to the action of the sulphur trioxide and sulphuric acid. The following reactions, represent in a general way the chloridizing action:

$$2NaCl + FeSO_4 = Na_2SO_4 + FeCl_2.$$
$$2NaCl + CuSO_4 = Na_2SO_4 + CuCl_2.$$
$$2NaCl + 2SO_3 = Na_2SO_4 + 2Cl + SO_2.$$
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The chlorine and chlorides thus formed react with the silver and silver sulphate to form the silver chloride:

$$FeCl_2 + AgSO_4 = 2AgCl + FeSO_4.$$
$$CuCl_2 + AgSO_4 = 2AgCl + CuSO_4.$$
$$2NaCl + AgSO_4 = 2AgCl + Na_2SO_4.$$
$$2HCl + 2Ag + O = 2AgCl + H_2O.$$
$$Cl + Ag = AgCl.$$

Any or all of these reactions may take place at the same time. The salt, reacting with the sulphates of iron and copper, converts those metals into their higher chlorides, while the chlorine and hydrochloric acid are formed at the same time. Both chlorine and hydrochloric acid, at the temperature of the roasting furnace, react readily with metallic silver or its sulphate, to form the silver chloride, while the chlorides of iron and copper, in chloridizing the silver, may pass repeatedly from the ferric and cupric condition to that of the ferrous and cuprous:

$$2FeCl_2 + 2Cl = 2FeCl_3.$$
$$2FeCl_3 + 2Ag = 2FeCl_2 + 2AgCl.$$
$$2CuCl + 2Cl = 2CuCl_2.$$
$$2CuCl_2 + 2Ag = Cu_2Cl_2 + 2AgCl.$$

The ferric chloride, $FeCl_3$, is volatile and at a red heat, chloridizes the silver with great avidity. The ferrous chloride at the same time is resolved into ferric oxide and ferric chloride:

$$3FeCl_2 + O_3 = Fe_2O_3 + 2FeCl_3.$$

In contact with aqueous vapor, and the fuel gases, at a red heat, the ferrous chloride may be converted into the magnetic oxide:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + 2H.$$

The magnetic oxide may be again reconverted into the ferric oxide, in the presence of salt and at a lower temperature, as was shown conclusively by Stetefeldt[1] who succeeded in converting an ore containing 67.2 per cent. magnetite to 1.4 per cent. after 4 1/2 hours' roasting with 5 per cent. salt.

Cupric chloride ($CuCl_2$) is easily decomposed at a red heat into cuprous

[1] Trans. A. I. M. E., 1885–1886.

chloride (Cu_2Cl_2) and free chlorine, which gives free chlorine available for the chloridization of the silver.

Arsenic and antimony form chlorides, which are easily volatile and which may be decomposed into arsenous and antimonous acids and chlorine and hydrochloric acid, by means of the oxygen, and the vapor from the burning fuel. These chlorides, however, will mostly escape without decomposition. If the temperature is low and the salt has not been added until the arsenic and antimony have been largely driven off, the soluble arsenates and antimonates, in the roasted ore, will not usually be present in sufficient quantities to seriously interfere with the extraction. If the raw ore contains arsenic and antimony in large amounts, much of the silver may be converted in the early stages of the roasting, into arsenate and antimonate. Ottokar Hofmann found in roasting arsenical ore that 53.8 per cent. of the silver was soluble in sodium hyposulphite, probably as arsenate of silver, before the salt was added to the ore.

Arsenous oxide volatilizes at 218° C. Chlorine, with the aid of heat, decomposes the sulphide of antimony completely, forming the trichloride of antimony and sulphur dioxide. The trichloride of antimony melts at 70° C.

Zinc.—Zinc blende, in oxidizing roasting, is converted into zinc oxide and zinc sulphate, while sulphur dioxide escapes. In the presence of salt, zinc blende remains indifferent and does not decompose salt, at least at the temperature used in chloridizing roasting. Salt does not decompose zinc sulphate. Zinc oxide may be converted into the chloride at a red heat. By the action of chlorine and hydrochloric acid zinc chloride is formed, which is very volatile. In ore which has been given a chloridizing roast, the zinc is usually found as the oxide, sulphate, and chloride. Zinc oxide, like the calcium and magnesium oxides, is completely soluble in acids, so that when an acid process is employed to extract copper or silver, zinc must be regarded more or less as equivalent to calcium and magnesium. In the chlorination of gold ores, when the chlorine is applied direct without the use of acids, considerable quantities of zinc will not seriously interfere with the treatment. Both zinc oxide and zinc sulphate react very slowly with chlorine.

Lead.—If galena is subjected to chloridizing roasting, especially in the presence of sufficient air, most of the lead is converted into sulphate, which does not react on the salt, and oxide, which may be converted into the chloride. Both lead oxide and chloride are volatile, while the sulphate remains indifferent. In the roasted ore, the lead will be in the form of sulphate and chloride, but the sulphate will predominate.

Calcium Carbonate.—Carbonate of lime, when roasted with metallic sulphides, will change partly into calcium sulphate and partly into the oxide (lime). The calcium sulphate does not act on salt, but the oxide

decomposes the metal sulphates and chlorides, and also, to some extent, the silver chloride. Calcium oxide, or carbonate, does not absorb chlorine when cold, but at a red heat combines with it to form calcium chloride, with the evolution of oxygen. If the ore contains calcium carbonate in large excess, only a small quantity of iron and copper sulphates will be formed, to decompose the sodium chloride. Most of the iron and copper sulphides in the ore will be converted directly into the oxides. Since the sulphates of iron or copper are necessary to release the chlorine in the salt, and these sulphates are not formed or are immediately appropriated by the lime, the salt will not react to release chlorine or hydrochloric acid, which are the most active elements in chloridizing roasting of copper, gold, and silver ores. The lime itself is quite indifferent to silver chloride at low temperatures, but decomposes it energetically when the temperature reaches red heat. If there are more sulphides in the ore than are necessary to convert the lime into sulphate or chloride, usually a good chloridization of the silver and copper may be obtained.

The practical effect of lime, in the formation of silver chloride, in chloridizing roasting, is clearly shown by a well conceived experiment by Ottokar Hofmann[1] on concentrates containing large quantities of sulphur, arsenic, iron, considerable zinc, some lead and aluminum. The object of the experiment was to ascertain the effect of varying quantities of calcium carbonate, in the formation of silver chloride, all other conditions remaining the same. The ore was roasted one-half hour with 7 per cent. salt.

Sample No.	Per cent. of concentrates in mixture	Per cent. of barren gangue in mixture mostly $CaCO_3$	Value of mixture per ton oz. silver	Value of leach tails per ton oz. silver	Chloridization per cent.
1	100		96.0	2.91	97.0
2	75	25.0	72.0	5.38	92.6
3	62	37.5	60.0	4.72	92.2
4	50	50.0	48.0	5.38	88.8
5	25	75.0	24.0	5.47	77.2

The deleterious effect of the lime is very evident from these results.

Magnesium usually occurs as the carbonate, and in chloridizing roasting, as in oxidizing roasting, has about the same effect as calcium. Magnesium carbonate is decomposed at 170° C. (338° F.) into magnesium oxide. If there are sulphides in the ore, much of the magnesium will be converted into the sulphate. The sulphate is quite infusible, melting only at about 1100° C. In chloridizing roasting the magnesium combines with the chlorine to form magnesium chloride ($MgCl_2$), with the liberation of oxygen. Magnesium chloride fuses at a red heat, 708° C. (1300° F.). Magnesium chloride is more positive in its action than sodium chloride.

Quartz.—Quartz is the most desirable gangue in chloridizing, as it is in oxidizing roasting. Silica is indifferent to any action in chloridizing roasting, unless perhaps, it promotes the formation of chlorides and oxides by catalytic action.

Barium sulphate, which occurs quite frequently associated with silver ores, remains inert during chloridizing roasting.

Alumina is not fused by heat alone, nor is it decomposed by chlorine at any temperature.

Sodium sulphate, so abundantly formed during chloridizing roasting, may be considered a neutral substance in any of the hydrometallurgical processes. It is usually filtered off before the solvent is applied.

Silver sulphate is completely decomposed by sodium chloride, at the temperature of the roasting furnace.

Percentage of Salt.—The percentage of salt used at various mills differs greatly, depending largely on the character of the ore, principally the gangue. More salt has sometimes been used than was really needed. Aaron when roasting a pyritic ore with 4 per cent. salt, found an enormous loss by volatilization; later he reduced the amount of salt to 3 lb. per ton of ore, and got satisfactory results. Ordinarily, the amount of salt for silver ores will vary between 1 and 5 per cent., although much greater percentages than these have been used. Only 3 per cent. was used at Panimint, California, and gave a chloridization of 95 per cent. The amount of salt is largely proportional to the amount of lime or magnesia in the ore. An excess of salt does not improve the chloridization.

If copper, instead of silver ores are to be chloridized, the amount of salt required will be larger. If the copper contained in the ore is considerable, the amount of salt will be roughly proportional to the copper. From 5 to 10 per cent. might be considered fair averages for ores containing only several per cent. of copper.

The minimum amount of salt that may be used for any ore is best determined by direct experimenting. First determine the conditions of time, temperature, and fineness of the ore, which will give the highest satisfactory chloridization with an abundance of salt, and then reduce it in successive roasts until a minimum is obtained which will show no appreciable difference as compared with the highest chloridization possible, with an abundance of salt.

Time of Adding Salt.—The time of adding salt is governed almost entirely by the composition of the ore. If the ore is low in sulphur, the salt may be added before the ore is charged into the furnace, preferably before it is crushed, so as to get an intimate mixture of ore and salt. If the ore contains considerable sulphur, combined with iron or copper, the ore may be given practically a full oxidizing roast before adding the salt, and still have enough sulphur in the ore to chloridize the silver. If

copper is to be chloridized, the ore should contain at least as much sulphur as copper before the salt is added. If the ore contains considerable zinc and lead sulphides, the sulphur combined with the zinc and lead may be disregarded for the purpose of chloridization, and the ore given an oxidizing roast previous to adding salt, if the sulphur combined with the iron and copper is large; if the sulphur so combined is small, the salt is best added at once to the raw ore.

If the ore is thoroughly oxidized, and does not contain sufficient sulphur, either as raw ore, or after a thorough oxidizing roast, the salt and pyrites, both finely ground, may be added to the ore. Ferrous sulphate may be used instead of pyrites, but is much more expensive.

If the salt is added while there is a large excess of sulphur in the ore, it will largely be volatilized without doing any good. If the salt is added at the proper time, the chloridization takes place very rapidly.

Heap Chloridization.—Imperfectly roasted ore, after being drawn from the furnace and placed in a mass on the cooling floor, or in a pit, will gain in chloridization, largely in proportion to the imperfectness of the roast. On very poorly roasted ores it may gain as much as 50 and 75 per cent. The reactions which take place in heap chloridization are essentially the same as those which take place in the furnace. In any well regulated mill, the ore is probably never so poorly roasted but that all the iron and copper sulphides are decomposed.

From the reactions given for chloridizing roasting, it is evident that air is not essential to the chloridization after the sulphides have been converted into the sulphates. Small quantities of air, however, permeate the mass and promote the reactions.

Ores which are well roasted in the furnace, and which is the only safe way to roast, do not show any increase in chloridization in the heaps, pit, or cooling floor.

If the ore does not contain lime in considerable quantity, moistening the hot ore adds to the chloridization of the silver and this is especially the case if the ore contains copper, or is moistened with a solution of cupric chloride. If the ore contains appreciable quantities of lime, then instead of adding to the chloridization, there is likely to be a diminution. A loss of chloridization of 10 per cent. has been known to occur in this way.

Composition of the Roasted Ore.—Ores which have been subjected to chloridizing roasting contain a great number of soluble salts. Of these, sodium sulphate, resulting from the decomposition of the salt, and the undecomposed sodium chloride, predominate. Besides these there may be the sulphates of manganese, zinc, copper, iron, aluminum, and magnesium; the chlorides of the same metals and of calcium and barium. The barium chloride will be immediately decomposed on solution, and precipitated as insoluble barium sulphate. Sodium arsenate is also

present if the ore contains arsenic. Salts not easily soluble in water, are cuprous chloride, lead chloride, calcium sulphate, sodium antimonate, and calcium oxide. Lead chloride, on solution, will be precipitated as lead sulphate. Silver chloride, lead sulphate, and antimonate are almost insoluble in water but are soluble in solutions of other chlorides. Cuprous chloride, calcium sulphate and calcium oxide are more soluble in a chloride solution than in water. If the ore contains large quantities of lime, the soluble metals may be precipitated as hydroxides.

The composition of Ontario raw ore, and of the ore roasted with 13 per cent. salt in a Stetefeldt furnace, from analyses made by Stetefeldt, is given by Kustel[1] as follows:

Raw ore	Per cent.	Roasted ore; shaft	Per cent.	Roasted ore; flue	Per cent.
Zinc	9.45	Zinc chloride	1.38	Aluminum chloride	1.07
Lead	6.07	Copper chloride	0.25	Sodium chloride	3.08
Iron	2.77	Aluminum chloride	1.51	Traces of chlorides of other metals.	
Copper	1.41	Sodium chloride	3.68	Aluminum sulphate	2.88
Manganese.	0.45	Traces of chlorides of other metals.		Lead sulphate	5.18
Silver	0.60			Sodium sulphate	10.01
Sulphur	7.68	Aluminum sulphate	0.56	Copper sulphate	0.74
Antimony.	1.20	Lead sulphate	3.26	Zinc sulphate	1.47
Arsenic	0.20	Sodium sulphate	4.62	Traces of sulphates of other metals.	
Silica	55.21	Traces of sulphates of other metals.		Rest, metallic oxides and gangue	
Alumina	13.14	Rest, metallic oxides and gangue.		Sulphur in undecomposed sulphides.	0.°64
Potassium sodium.	1.00	Sulphur in undecomposed sulphides.	0.18		
Bismuth	trace				
Cadmium	trace				
Lime	trace				
Magnesia	trace				

These results are interesting as showing the condition of the various constituents of the ore, after chloridizing roasting.

Of the silver contained in the ore, 81.32 per cent. was chloridized.

Volatilization of the Silver.—The volatilization of the silver, in chloridizing roasting, is largely due to the presence of other chlorides which are more volatile than the silver chloride. The volatilization of the silver is roughly proportional to the volatilization of the base metal chlorides, or to the loss in weight the ore sustains. Manganese seems to be particularly active in causing loss by volatilization. Cupric and cuprous chlorides, both of which volatilize at a low heat, are likely to cause a heavy loss of silver. Arsenic and antimony are also effective in assisting the volatilization of the silver chloride. A high temperature indirectly causes a high loss of silver by the expulsion of the volatile chlorides.

Much of the loss due to volatilization, is chargeable to the manipula-

[1] Kustel, "Roasting of Gold and Silver Ores".

tion of the ore in the furnace. Any condition which will produce the chloridization of the silver, if carried to excess, will also cause its volatilization. Silver chloride, under the conditions of roasting, is formed at a comparatively low temperature by the chemical reaction between the salt and sulphates. A scarcely visible red heat is quite sufficient for these reactions, and if this temperature is not exceeded, only a small loss by volatilization will occur. If, however, the temperature is elevated to, say, a bright red, a high loss of silver is sure to take place. A safe rule to follow, is to keep the ore at the lowest possible temperature at which it will give off visible fumes. It is best to maintain a deep layer of ore, and plenty of air. A small charge of ore spread thinly over a large hearth area, will show a greater loss by volatilization, than a large charge with a deep bed spread over the same area.

The stirring of the ore should not be too frequent, but this is not an essential if the temperature is not too high. These conditions for good chloridizing roasting are contrary to those desirable in the best oxidizing roasting, where the ore should be in a thin layer and be stirred as frequently as possible. Chloridizing roasting can be done with a very small loss by volatilization—frequently only an inappreciable loss—and it is very probable that the great losses recorded are due entirely to improper manipulation.

In the chloridizing roasting of any ores, at an exceedingly low temperature, a difficulty may arise, in the subsequent chemical treatment. If roasted at too low a temperature, some of the injurious elements may not be decomposed sufficiently, so that trouble may arise in the consumption of chemicals when the solvent is applied to the ore. This, however, is a matter for adjustment for each particular ore, and will usually, in such cases, resolve itself down to roasting at the highest temperature the ore will stand without serious loss by volatilization.

Almost any ore, likely to be treated by a solvent process, can be effectively chloridized, but the essential of such roasting is that the loss during the process should not be serious, or if serious, its recovery should be carefully considered. With care, many silver ores can be given a chloridizing roasting with not much greater loss of silver than in oxidizing roasting.

That there is sometimes a considerable loss of silver in oxidizing roasting is pretty well established. Plattner in his "Metallurgische Rostprozesse" goes very minutely into the loss of gold and silver in oxidizing roasting. By a series of muffle roasts on a small scale, he comes to the conclusion that while there is no loss of gold, the loss of silver is unavoidable. From numerous tests, varying from 3/4 to 1 1/2 hours he records a loss of from 0.5 to 18 per cent. of the silver. He concludes that the percentage loss of silver increases with the temperature, the porosity of the charge which facilitates the supply of air throughout the ore mass, the

freedom of the silver from combination with other substances, and with the time of the roasting.

In order to verify the work done by Plattner, Christy[1] cites some experiments in oxidizing roasting made by himself and others. The material used in the experiments were concentrates from Nevada City, California, which consisted chiefly of pyrite, with small amounts of chalcopyrite (0.05 to 1.5 per cent. Cu), a little galena, a small amount of quartz, traces of arsenic and antimony, but no tellurium. The ore was given an oxidizing roast of from 1 1/2 to 8 1/2 hours; in the early stages at incipient dull red, and finished at dull red to full red. The results are tabulated as follows:

Time of roasting, hours	Raw ore, ounces per ton		Roasted ore, ounces per ton		Percentage loss per ton	
	Gold	Silver	Gold	Silver	Gold	Silver
1 1/2	4.58	27.50	4.58	26.44	0.00	3.85
2 1/2	4.58	27.65	4.58	27.07	0.00	2.09
8 1/2	4.50	28.39	4.50	27.39	0.00	3.52

These results verify the conclusion of Plattner and others, that while no loss of gold occurs in oxidizing roasting, by volatilization, the loss of silver may be considerable.

Butters[2] found in roasting a hard white quartz, intimately mixed with about 7 per cent. calcite and a very little pyrite, assaying 5.55 oz. silver and 0.65 oz. of gold, per ton, that there was a loss by volatilization in oxidizing roasting, of 2 to 9 per cent. of the silver, but none of the gold.

It is possible that losses of silver, which have been attributed to chloridizing roasting may have been partly due to the loss in oxidizing roasting, and especially if some of the silver in the ore is in the form of chloride.

Volatilization of the Gold.—It is pretty well established both by carefully conducted experiments and by the experience of practical metallurgists, that no loss of gold takes place either in oxide or sulphide ores, in oxidizing roasting. There seems to be some doubt in the case of tellurides, but the experience with Cripple Creek ores, containing tellurium, of which hundreds of tons are roasted daily, is, that no appreciable loss, if any at all, occurs by volatilization. Kustel records a loss of 20 per cent. of the gold during the oxidizing roasting of certain telluride ores of gold and silver, and states that this is not a mechanical but a volatilization loss. There can be no doubt about the gold, combined with tellurium,

[1] Trans. A. I. M. E., 88–89.
[2] Trans. A. I. M. E., 88–89.

volatilizing at elevated temperatures, but whether any volatilization takes place at the low temperatures and under the practical conditions of roasting, seems very doubtful.

Tellurides, even in small quantities, are extremely sensitive to chlorine at almost any temperature, at which salt is decomposed. Experience with Cripple Creek ores, in large 100-ton furnaces, showed appreciable loss of gold when only a very small amount of salt—from 1/2 to 2 per cent.—was added during the roasting. A loss was shown even when the salt was added to the hot ore dropping on the cooling hearth.

Many ores are known to contain chlorine, frequently as chloride of silver or chloride of lead. That ore containing a part of its silver as chloride, if given an oxidizing roast, will volatilize small amounts of both gold and silver, was proved conclusively by the author in exhaustive tests on Tonapah ore. It is probable when gold losses occur in any ore in oxidizing roasting, and especially in the tellurides, it may be due to small quantities of chlorine.

Prof. Christy[1] made some interesting experiments on the volatilization of gold in the chloridizing roasting of pyritic ores. As the result of a large number of experiments he comes to the following conclusions:

At 100° C. (212° F.) the volatility of the gold in an atmosphere of chlorine, is almost zero; that the loss begins, above this temperature, to rapidly increase to a maximum at a temperature of about 250° C. (482° F.); that it rapidly diminishes to a temperature somewhere below red heat; that it again increases, but more slowly, to another maximum, at a temperature above a melting heat, and that this increase is apparently continuous between a red heat and a white heat. The ratio of losses at various temperatures is also instructive; at incipient redness the standard loss is already 0.05 per cent.; at a cherry red it is five to seven times as great as at incipient redness; at incipient yellow it is more than eight times what it is at incipient red; while at melting heat it is nearly thirty times as great.

Crosly[2] found with a certain California pyritic ore, assaying about $110.00 in gold, and $40.00 in silver, that an oxidizing roast showed no appreciable loss, but when the salt was added, losses appeared rapidly. Thus, according to his tests, with 3 per cent. salt the gold loss was 30 per cent. and the silver loss 50 per cent. of the assay value. He attributed the loss to the presence of tellurides, which he supposed were present.

Aaron[3] found a large loss in roasting a simple pyrite in a 3-hearth reverberatory furnace, with 1 to 2 per cent. of salt, which was added on account of the silver. He then made two tests on a small scale;

[1] Trans. A. I. M. E., 1885.
[2] Trans. A. I. M. E., 1888.
[3] "Leaching Gold and Silver Ores," 1881.

one with 4 per cent. salt, the other without any salt, and purposely pushed the roasting to an extreme as to time and temperature, and found on assaying that the salted ore contained less than half as much gold as the unsalted one. He also found that the ore, in roasting, sustained a loss of 18 per cent. in weight, and consequently should have assayed 18 per cent. more than the raw ore, which was not the case. By modifying the roasting, so as not to add the salt until the dead roasting of the ore was finished, not only did the roasted ore assay 20 per cent. more than the raw ore, but the yield overran the guarantee, while the tailings, nevertheless, contained considerably more gold than before. He afterward found that a very small quantity of salt—not more than 3 lb. per ton of ore—might be mixed with the raw ore without detriment to the gold and with decided advantage to the extraction of the silver.

The principal object of roasting gold ores, containing silver or copper, with salt, is to chloridize the small amounts of silver and copper, and in some cases to neutralize substances in the ore, which might be injurious to the solvent. By a partial chloridizing roast, or even with an oxidizing roast, it is practicable to get a high extraction of both the gold and silver by either the cyanide or chlorination processes. If it is simply a matter of neutralizing injurious substances in the ore, this can be done in chloridizing roasting by not pushing the operation to the limit, and if not carried beyond the point required to satisfy the base elements, no appreciable volatilization of either gold or silver will occur.

Chloridization of Copper Ores.—According to Von Kothny[1] by roasting copper sulphide mixed with iron oxide and sodium chloride practically all the sulphur goes into sulphate and about half the copper is transformed into chloride. Anhydrous cupric chloride mixed with sodium chloride and heated in a current of air to 250° C. gives off chlorine. The decomposition of copper sulphate by sodium chloride begins at 280° C. Ferric chloride converts copper oxide into chloride very rapidly at temperatures from 500 to 600° C. The formation of copper sulphate by roasting with copper oxide in the presence of sodium chloride plays no part. At temperatures of 300 to 600° C. ferric sulphate converts copper oxide slowly into sulphate. Chlorine is without direct action on cuprous sulphide. The reactions involved in the Hargreaves process by which hydrochloric acid is formed plays no part in converting cupric oxide into chloride. Von Kothny concludes that the mechanism of the chloridizing of pyrite cinder containing a small amount of copper and sulphur, is as follows: The copper is present largely as sulphide, which by an oxidizing roasting is converted into sulphate and oxide. Sodium chloride acts directly on the sulphate and ferric chloride on the oxide. To insure chloridizing of such material it must be finely

[1] *Metallurgie*, July 8, 1911.

ground; a large amount of air must be admitted in the oxidizing roasting period and stirring must be resorted to to insure contact with oxygen; sufficient pyrite must be present to furnish the required amount of ferric chloride and is best added in a weathered form; for 4 per cent. copper content at least 7.5 per cent. salt must be added; the process should be carried out at temperatures between 500 and 600° C. For a full discussion of chloridizing roasting of copper ores see "Longmaid-Henderson process," Part II, page 246.

Principal Factors in the Loss of Silver, Gold, and Copper by Volatilization.—The principal factors, controling the loss of silver, gold and copper by volatilization, in chloridizing roasting, have been well established both by practice and careful experiments. These, in the order of their importance, are:

1. Temperature.
2. Time.
3. Amount of air, or surface exposed.

The amount of salt has some influence on the volatilization, but it is supposed that the amount of salt used is the least that will give satisfactory results, and once determined, becomes constant.

The presence of volatile substances, such as arsenic, antimony, selenium, tellurium, and the chlorides of copper and iron, also affect the volatilization. Gold is particularly sensitive to tellurium in chloridizing roasting. But as these are constituents of the ore, they cannot be considered as variable, or controllable factors, except in so far as preliminary oxidizing roasting may eliminate them.

Temperature is the all important factor in chloridizing roasting. Any ore chloridized at an excessive heat will volatilize much of the metals, irrespective of any considerable time, or in any atmosphere attainable in a roasting furnace. If the temperature is kept at the lowest possible point at which the metals can be chloridized, then the time of roasting and the amount of oxygen in the furnace atmosphere is immaterial. By merely changing the temperature, from 10 to 80 per cent. of the metals may be volatilized in a short time; or only a few per cent. may be volatilized after several hours roasting, all other conditions remaining the same.

Russel, experimenting with Ontario ores, found a volatilization of 8.3 per cent. of the silver at a dark red heat, and of 17.6 per cent. at a cherry red. Ottokar Hofmann[1] found in roasting calcareous ores containing large quantities of zinc and arsenic, that the ore lost 3.5 per cent. of its weight and 1.8 per cent. of its silver was volatilized when roasted at a low temperature; the same ore roasted at a high temperature with insufficient air, lost 7 to 13 per cent. of its weight, and 15 to 25

[1] Min. Ind., 1896.

per cent. or more of the silver. He also found[1] on an ore consisting essentially of 25 per cent. zinc, 12 per cent. lead, 21 per cent. sulphur, 7 per cent. iron, and 10 per cent. calcium carbonate, that the loss by volatilization varied from 1.7 to 15 per cent. The least increase of temperature above a dull red, caused a heavy loss, even if the increase lasted for only a short time. The average of 31 days roasting at a high (almost white) heat was:

Chloridization of the silver, 72.7 per cent.
Loss by volatilization, 17.9 per cent.

Roasted at a low heat (not above a dull red):

Chloridization of the silver, 81.5 per cent.
Loss by volatilization, 1.2 per cent.

The chloridization in favor of the lower heat was 8.8 per cent. and a decrease of loss by volatilization of 16.7 per cent.

Time.—The volatilization of the silver, gold, and copper, in chloridizing roasting, is approximately proportional to the time of roasting, other conditions remaining the same. If in chloridizing roasting, an ore will lose, say 1 per cent in the first hour after the salt is added, it will lose approximately 5 per cent. after five hours roasting, if the conditions remain the same.

Air or Oxygen.—Time and temperature remaining the same, the volatilization will be approximately proportional to the amount of air supplied to the ore. If a ton of ore is roasted on a hearth area of 100 sq. ft., shows a volatilization of say, 1 per cent. per hour, it is likely to show 2 per cent. per hour if spread over a hearth area of 200 sq. ft.

Experiments as Compared with Practice.—Almost all the chloridizing roasts made in preliminary tests, in a muffle, will show a higher loss by volatilization than will subsequently be found in practice. There is no appreciable loss in heap chloridization, when improperly roasted ore is withdrawn from the furnace and the chloridizing allowed to proceed on the cooling floor. Neither does any appreciable loss occur when the damper of the furnace is closed, so that the furnace has no draft and no fresh air supply.

Relation of Sulphur to the Chloridization of Silver and Gold.—Chloridization of the silver, in chloridizing roasting, may take place very rapidly under proper conditions. If the ore contains an excess of sulphur, chloridization will not take place to any appreciable extent, until some of the sulphur has been eliminated, even if there are sulphates present. This may be due to the reducing action of sulphur dioxide, or other reducing gases, which are likely to occur in abundance in the early stages of the roasting.

[1] *Engineering and Mining Journal*, 1888–89.

In order to determine the relation of the chloridization of the silver and gold to the sulphur, and the progress of chloridization during the roasting, the following interesting results were obtained by the author on Tonapah concentrates, which consisted largely of silica and iron pyrites, about 3 per cent. lead, and small quantities of zinc, copper, manganese, and antimony. The raw ore had 16.35 per cent. sulphur, and assayed 615.0 oz. silver, and 6.50 oz. gold per ton. The roasting was done in a furnace having a hearth area of 100 sq. ft. The concentrates were first given an oxidizing roast for two hours, after which 10 per cent. salt was added and samples taken every hour.

Time, chloridizing roasting	Sulphur, per cent.			Roasted ore, value ounces		Hypo tails, value ounces		Chloridization, per cent.	
	Total	Soluble	Insoluble	Silver	Gold	Silver	Gold	Silver	Gold
0 hours.....	16.35			615.0	6.50				
1 hour.....	9.45	3.00	6.45	610.0	6.45	689.2	7.30		
2 hours.....	7.10	4.65	2.45	612.0	6.60	700.0	6.80		
3 hours.....	6.65	5.32	1.33	610.0	6.35	420.0	6.00	31.7	7.1
4 hours.....	6.45	5.60	0.85	580.0	6.29	140.0	5.80	77.2	10.5
5 hours.....	6.25	5.70	0.55	580.0	6.13	78.0	3.40	87.7	47.4
6 hours.....	6.15	5.80	0.35	575.0	6.00	29.8	3.00	95.5	53.6

It will be noticed that no chloridization took place the first 2 hours of chloridizing roasting, notwithstanding that there was from 3.0 to 4.65 per cent. soluble sulphur in the ore at that time. The same results in chloridization would doubtless have been obtained if the salt had been added three hours later than it was, or after the ore had been given an oxidizing roast for 5 hours.

The high value of the hypo tails after 1 and 2 hours chloridizing roasting, is due to the fact that there was no silver chloride formed, and in leaching with the hypo the soluble matter was removed, thereby somewhat concentrating the value of the ore.

The high soluble sulphur in the roasted ore is mostly due to the sodium sulphate formed by the roasting. Some of the insoluble sulphur may have been in the form of lead or calcium sulphate.

Determination of Loss by Volatilization.—In order to roast skillfully it is of great importance to frequently ascertain the loss by volatilization, but to do this it is necessary to know the loss of weight the ore sustains. In practical handling of the ore this is difficult and inconvenient. Hofmann[1] gives the following method, which can be performed in an assay office in a few hours:

"Ten grams of the raw pulp, containing the same percentage of salt as the ore in the furnace, is placed in a roasting dish and roasted in the

[1] "Hydrometallurgy of Silver," Page 22.

muffle for half an hour or an hour; then the sample is removed from the muffle, allowed to cool, weighed, returned to the muffle, roasted again for half an hour, and then weighed again. This is repeated until two weighings are alike, or until in the last half hour the ore does not lose more than 2 or 3 mg., then the difference between the original weight and that of the last weighing, expressed in percentage, gives the highest possible loss the raw ore can suffer.

Ten grams of a sample of roasted ore, corresponding with the sample of raw pulp, is placed in a roasting dish, and also roasted in the muffle until two weighings agree, or the difference between two consecutive weighings is not more than 2 or 3 mg. The difference between the first weighing (10 grm.) and the last, expressed in percentage, gives the weight which the roasted ore is still capable of losing if subjected to prolonged roasting. If we deduct, therefore, the capable loss from the highest possible loss, we obtain in percentage the loss in weight the ore has suffered during roasting in the furnace by volatilization."

Chloridization Determination.—To determine the amount of silver and gold chloridized, it will usually be sufficient for practical purposes to take several ounces of an average sample of the ore, and treat it thoroughly with a solution of sodium hyposulphite. It will be found most satisfactory to put the ore and hypo in a beaker for several hours at least, stirring it occasionally, and then thoroughly filter and wash the ore in a funnel. It is then dried, bucked, and assayed. If the ore contains large quantities of soluble salts, the sample should be weighed before and after the hypo treatment, and the difference allowed for in the results of the assay.

Chloridization determinations are sometimes made by taking an assay ton, or less, of the ore treating it with hypo, and assaying the residue. While this rectifies any error of soluble salts, it introduces a more or less uncertain element in the assaying.

CHAPTER V

PYROMETRY

Color Names of Temperatures.—The temperatures corresponding to different colors have been determined quite accurately by White and Taylor, by Howe, by Janivier, and by Pouillet. The difficulty in determining a certain temperature, by its corresponding color, lies in the personal equation of the observer and the time and conditions of observation. Much depends on the susceptibility of the retina of the observer to light as well as the degree of illumination under which the observation is made. A furnace looks very much hotter at night than at day, and hotter in a dark room than in a bright one. The most experienced roasterman is unable to compensate fully for these factors, nevertheless, the information given by these color temperatures is often convenient.

White and Taylor			Howe		
Name of color	Temperature		Name of color	Temperature	
	C.	F.		C.	F.
			Lowest red visible in the dark.	470	878
			Lowest red visible in daylight.	475	887
Dark red, blood red, low red.	566	1,050	Dull red	550	1,022
Dark cherry red	635	1,175		625	1,157
Full cherry red	746	1,375	Full cherry	700	1,296
Light cherry, bright cherry, bright red.	843	1,550	Light red	850	1,562
Orange	899	1,650			
Light orange	941	1,725			
Yellow	996	1,825	Full yellow	950	1,742
Light yellow	1,079	1,975	Light yellow	1,050	1,922
White	1,205	2,200	White	1,150	2,102

(*E. and M. J.*, Jan. 20, 1900.)

Pouillet			Janivier		
Name of color	Temperature		Name of color	Temperature	
	C.	F.		C.	F.
Incipient red	525	977	Very dull red	525	977
Dull red	700	1292	Dull red	700	1292
Incipient cherry red	800	1472	Bright red	800	1472
Cherry red	900	1652	Cherry red	900	1652
Clear cherry rod	1000	1832	Bright cherry red	1000	1832
Deep orange	1100	2012	Very deep orange	1050	1922
			Deep orange red	1100	2012
Clear orange	1200	2192	Orange red	1200	2192
White	1200	2372	Whitish	1300	2372
Bright white	1400	2552	Brilliant white	1400	2552
Dazzling white	1500 to 1600	2732 to 2912	Dazzling white	1500	2732
			Blue white	1600	2912

(*E. and M. J.*, July 20, 1905.)

Pyrometric Determinations.—The only way of accurately determining the temperatures in various parts of a roasting furnace, under all conditions, is by the use of reliable pyrometers, and every roasting plant should be equipped with at least one of these instruments.

Attempts have frequently been made to get uniformity in the quality of ore, roasted for treatment by the chemical processes, by establishing a system of absolute temperatures in certain parts of the furnace, and so firing as to keep those temperatures constant. On theoretical grounds this appears quite feasible. The difficulty lies in assuming that the ore fed into the furnace is of uniform quality, and that the other essential factors, such as air supply, always remain the same. Ore which is well bedded, and containing about 2.5 per cent. sulphur, may vary as much as 0.35 per cent. to 0.50 per cent., in 24 hours. The conditions which would be ideal for ore having 2.25 per cent. sulphur would be far from ideal for ore having 2.50 or 2.75 per cent.

Much also depends on the physical and chemical composition of the ore. The condition of temperature which would give the best results for partly oxidized ore would not give satisfactory results with ore containing the same amount of sulphur, from the deeper workings of the mine, in which no oxidation had taken place, assuming of course, that the amount of ore roasted remains the same. When ore contains an excessive amount of dust, it cannot be roasted at the same rate and at the same temperature as ore which contains only the normal quantity, and the dust is likely to vary, especially when the supply bins get low.

The temperature of a roasting furnace appears to be very much hotter at night than during the day. Inexperienced roastermen are

frequently misled by this, and even experienced men cannot judge accurately within the desired limits. The tendency in the daytime, especially in well lighted buildings, is to get the temperature too high, and at night to get it too low. In such cases pyrometers are of great service in establishing temperatures. They are also of great service in determining the temperature beyond which it is unsafe to roast. Experience and skill in the appearance of the ore as it progresses through the furnace, and its appearance after roasting, however, are the best general guides to obtaining uniform results. It is questionable whether, even with a perfect system of pyrometry, the experience and skill of the operator will not always remain the dominant factor.

It is a curious fact that when furnaces are overheated, the amount of sulphur in the roasted ore is abnormally high. One of the dangers in employing new roastermen is, that in their anxiety to get a good roast, they invariably fire at too high a temperature, with the result, that the roasted ore contains an unusually large amount of sulphur, partly fused, and is in the worst possible condition for treatment by a solvent process. Overheated partially roasted ore is also likely to run more or less like a liquid and in this way emerge insufficiently roasted. Pyrometers, in such cases, are invaluable as a warning to the roasterman when the safe limit of temperature is being exceeded. Frequently pyrometric determinations are essential to intelligent work, but they must be supplemented by experience and skill, and not dominate them.

Of the pyrometers in general use, those of the Le Chatelier type will be found most satisfactory in roasting work. If the thermo-electric couple is protected, it may be inserted into the furnace and kept there a very long time—in fact more or less permanently—without appreciable injury. The limit of temperature at which it is safe to use these pyrometers is a little below the melting point of platinum, which is about 3250° F., although readings above 3000° F. cannot be relied upon as perfectly accurate. In roasting work these temperatures are never approached. It is rarely that 1700° F. (927° C.) is exceeded. From 1400° F. to 1600° F. (760 to 871° C.) is the usual range in the hottest part of the furnace, for the various ores. Frequently ores are encountered which give the best results at as low a temperature as 1000° F. (528° C.). It will be seen, therefore, that the only danger to the thermo-electric couple of the pyrometer is from the furnace gases. Even this danger is remote in any case, and is entirely obviated if the thermo-electric couple is protected.

Several pyrometers inserted at various points of a large roasting furnace will give invaluable information as to the limits of temperature, which for any particular ore, will give the best extraction. Once these extreme limits have been determined, it is an easy matter to fire the furnace so that they shall not be exceeded.

While the determination of the absolute temperatures in roasting is not essential, nevertheless it is highly desirable. One of the gratifying features of the Le Chatelier type of pyrometer is, that absolute temperatures may be determined with greater facility and accuracy than the relative temperatures may be determined by other means, and absolute temperatures are always reliable for comparison.

The elements of a Le Chatelier pyrometer consist:

1. Of a thermo-electric couple, which generates, when heated, a slight electric current, which is proportional to the heat applied.

2. A galvanometer so arranged that the deflection of the needle, due to the current, indicates the temperature on the scale of the galvanometer.

3. Flexible wires connecting the thermo-electric couple with the galvanometer.

In using the pyrometer, the thermo-electric couple may be inserted directly into the furnace at the points where the temperature is desired, and the reading taken. Such a proceeding is awkward and troublesome. When only one galvanometer is used, the most satisfactory arrangement is to permanently insert the thermo-electric couples at the various points of the furnace, as desired, and by small switches and the wires connecting the couples with the galvanometer, the temperatures of the furnace at the different points may be quickly determined. In the same way, the temperatures of different furnaces may be readily ascertained. The galvanometer should be located at a convenient point, away from the dust and fumes of the furnace room. The thermo-electric couples may be inserted into the furnace through the arch, but care must be taken not to project them down far enough to be injured by the rabbles, although it is desirable to get them as close to the ore as possible. The thermo-couple, where it is intended to remain permanently in the furnace, should be protected by porcelain tubes.

If a continuous record of the temperature at any one point is desired, it is best to use a recording pyrometer. This consists essentially of:

1. A recorder, which is composed of a galvanometer and a clock arrangement, so that a pencil indicates the temperature and time on a moving chart.

2. The thermo-electric couple, the fire end of which is inserted into the space, where the temperature is to be measured.

3. Flexible wires connecting the recorder with the thermo-couple.

With this apparatus, a continuous, automatic, and permanent record of temperature and time may be made, which will give an accurate idea of the firing of the roasterman during the entire shift. A comparison of charts, will quickly establish the best temperature at which it is desirable to roast any ore, and locate the responsibility of any defects in the ore due to the temperature in roasting.

CHAPTER VI

ROASTING FURNACES

Roasting furnace design as applied to roasting ores preparatory to treatment by the hydrometallurgical processes, is rapidly resolving itself down to the various types of mechanical reverberatories. Hand reverberatories are still in use in small reduction works, but even for small output they are rapidly being displaced by the more efficient mechanical roasters. Labor, in hand roasting, has been the most important factor in the cost of operation, especially in mining districts, where labor is from $2.50 to $4.00 a day. Besides, the quality of labor is an exceedingly variable factor, and as the quality of a roast depends much on the efficiency, conscientiousness, and skill of the workmen, it is a disturbing element in any metallurgical plant where hand roasting is used.

The tendency, therefore, has been to eliminate the labor item, and the personal factor, by the substitution of mechanical for hand furnaces. A mechanical furnace, once set in motion under the conditions which by experiment have been found to give the best results, will always give practically the same results if the same conditions are maintained, and it is possible to keep the conditions practically constant. The personal factor of the workmen, in mechanical furnaces, is largely though not entirely eliminated. Maintaining proper conditions in a roasting furnace requires skill, but as the extremely hard labor of hand rabbling the ore is eliminated in mechanical furnaces, there is not the same temptation to slight the work.

The output per shift is very much larger in a mechanical than in a hand furnace, so that it makes it possible to pay the men better and get a superior quality of labor. In mechanical furnaces, the principal factor under the control of the roasterman, is the temperature of the furnace, and even this may be made largely automatic by the judicious use of pyrometers. The principal function of the roasterman, in large mechanical roasters, is that of an overseer, and to regulate the temperatures as indicated by the pyrometers.

Wonderful strides have been made in roasting and in mechanical roasting furnaces in recent years. Roasting can no longer be considered either difficult or expensive if fuel is available at a reasonable price. Roasting costs of ten or twenty years ago, in hand furnaces, or even in mechanical furnaces, are now obsolete, and the future will see still further reductions.

The mechanical difficulties of roasting furnaces, prevailing some years ago, which are peculiar to mechanism working under high temperatures and in the presence of dust, have been practically overcome in all of the successful mechanical furnaces now in use. It is not unusual for a large 100-ton mechanical roaster to run from three to six months without a single shut-down except, perhaps, the stopping of the mechanism for some minutes to change the rabbles; but this does not interfere with the daily output of roasted ore. It is not unusual for a furnace to run from six months to a year without cooling for repairs.

Roasting, in mechanical furnaces, is better and cheaper than in any type of hand furnace, whether the amount roasted is from 5 to 10 tons a day, or from 100 to 200 tons, for a single furnace. The capacity of 200 tons has not yet been realized, nevertheless, there are no mechanical or chemical difficulties to its realization. Roasting furnaces of that capacity, in large works and on low grade sulphur ores, will soon be an established fact, and will considerably reduce present costs of roasting. It is not now unusual, on Cripple Creek ores containing from 1 to 3 per cent. sulphur, to roast 125 tons a day in furnaces designed to roast, normally, 100 tons. Since it usually takes one man on a shift to attend to a mechanical roaster, whether the capacity is 25, 50, or 100 tons a day, the saving in the larger units is manifest, as well as the saving in fuel and other items. If the furnaces are fired with oil, or with well designed centralized gas producer plant, one man on a shift can attend to several furnaces, irrespective of their size, with an extra man occasionally to assist in attending the producers and changing the rabbles.

In small installations, the first cost of a mechanical furnace, over a long reverberatory, is not usually a serious item. The difference need not exceed $3000 to $3500 and the cost of roasting can usually be reduced from 50 to 75 per cent. A good mechanical furnace to roast, say, 10 tons of pyritic concentrates a day, or 25 to 30 tons of low sulphur silicious ore, can be erected for about $6000. It will take three of the ordinary long hand reverberatories to do the same work. Three such furnaces would cost more than the mechanical furnace, and would require one man on a shift for each furnace, making nine men in all; whereas the mechanical furnace would require only one man on a shift, or three men in all. As the amount of ore roasted per day becomes larger, the difference in cost of roasting, between the mechanical and hand furnaces, becomes more pronounced.

The variety of roasting furnaces, evolved and suggested, have been numerous. The practice has all been toward greater simplicity. Of the hand reverberatories, the multiple hearth, for roasting ore for subsequent treatment by chemical processes, has become obsolete. The "Long Reverberatory," the "Fortschauflungsofen" of the Germans,

has supplanted all other types of hand furnaces, and proved itself the survival of the fittest.

The furnaces to consider most seriously in the treatment of copper, gold, and silver ores by the solvent processes, are:

Hand reverberatories,
Mechanical reverberatories,
Revolving cylindrical furnaces,
Muffle furnaces.

All of these types are in actual and successful use. Shaft furnaces, like those of the Stetefeldt type, have long since become obsolete. There are none now in operation, and it is questionable whether a roasting furnace, based on that principle, can ever be devised which will successfully compete with the various types of mechanical reverberatories. The chemical conditions of roasting in a shaft furnace are all that could be desired, but the physical and mechanical difficulties are well-nigh insurmountable.

Hand Reverberatories.—A hand reverberatory roasting furnace, fired with solid fuel, consists essentially of a hearth, a fire-box, a bridge separating the hearth from the fire-box, a reverberatory arch over the hearth and which reverberates the heat and flame toward the hearth, a flue, and means, such as exhauster or chimney, of acquiring a draft through the furnace. If gas or oil are used as fuel, the fire-box and bridge may be dispensed with, and the gas or oil injected through the side walls or through the arch.

A hand reverberatory is one in which the ore is stirred and advanced by hand labor; in a mechanical reverberatory the ore is stirred and advanced by mechanical means.

The hand reverberatories may be subdivided into two general classes, based essentially on the method of operation. These are:

1. The short reverberatory, in which the ore is all charged, roasted, and withdrawn, in successive complete operations.

2. The long reverberatory, in which the ore is charged at one end, and then advanced by stages, while at each stage another charge is introduced and one withdrawn. Several charges are, therefore, in the furnace at the same time and each going through its cycle of treatment, independent of the others.

Short Reverberatory.—This type of reverberatory is used only in works where small quantities of ore are treated. These furnaces, while cheap to construct, are expensive to operate. They labor under the disadvantage that the conditions of the furnace itself change as the ore progresses in the roasting operation; while in the long reverberatory the conditions of the furnace remain practically the same all the time, but as

the ore progresses in the roasting it is advanced against the purer air and more highly oxidizing atmosphere.

Figs. 1 and 2 show section and plan respectively of a short reverberatory, which is the usual form and construction for furnaces of that size. It has a hearth area of approximately 120 sq. ft., and is capable of roasting a ton of ore at a charge. The number of charges that can be roasted in 24 hours depends upon the ore; if the ore is silicious and low in sulphur, three charges a day can be roasted; if the ore consists of pyritic concentrates, from one to two charges a day is about all that could be put through. If the hearth is made longer than 12 ft., it is better to throw the arch longitudinally over the hearth, instead of transversely, as shown.

In Figs. 1 and 2, *A* represents the hearth, *B* the reverberatory arch, *C* the fire-box, *D* the bridge wall, *E* the flue holes leading from the reverberatory chamber to a small flue chamber before entering the stack,

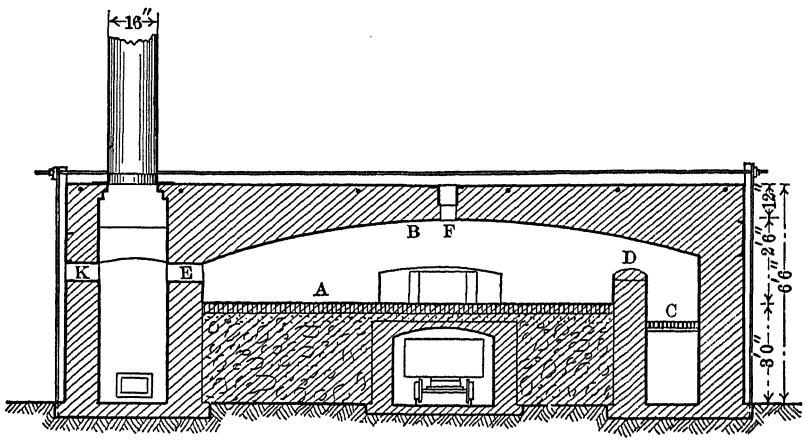


FIG. 1.—Short hand reverberatory. Longitudinal section.

F the charging hole through the arch from the top of the furnace, and *H* a hole through the hearth for discharging the roasted ore through a spout on to the cooling floor, or into a car or wheel-barrow, to be taken to the cooling floor. The flues, *E*, are arranged so that the flame from the fire can be equally distributed over the entire body of ore on the hearth. The holes, *K*, in the outer wall, easily admit of the regulation of the flue holes by means of bricks placed in the flues. The stack, also, should be provided with a suitable damper.

It is not necessary to build the entire interior of the furnace of fire brick. The fire-box, bridge, and arch immediately over them must be built of fire brick; the rest may be built of any good common red brick, preferably a pressed brick of the cheaper quality. Common pressed brick for the hearth is very desirable; it is hard enough to withstand the wear, and smooth and even enough to make the rabbling easier than it

would be otherwise. The hearth brick should be set on edge, 4 in. thick, and laid without mortar. The joints may afterward be filled in with fine sand or tailings.

On account of the bridge being exposed to injury by the high temperature on one side, and by rabbling on the other, it is desirable that the top course should be made of fire clay tile, say, 12 in. by 24 in. by 2 in. thick. The grates are 12 to 16 in. below the top of the bridge, and the top of the bridge is 8 to 10 in. above the hearth. Through the middle of the arch is an opening of cast iron, *F*, with a well-fitted cast-iron cover, through which the ore is charged into the furnace. The walls of the furnace should be reasonably thick, in order to retain the heat as much as possible,

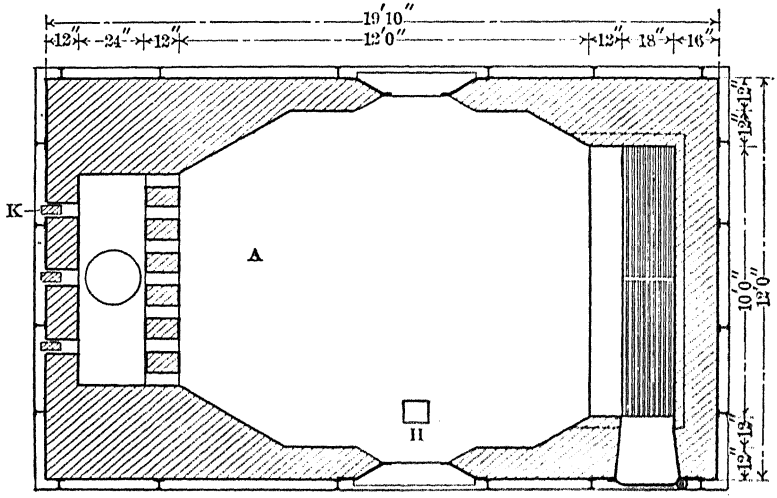


FIG. 2.—Short hand reverberatory. Plan.

and to prevent the furnace-room from getting uncomfortably hot. The arch should be at least 8 in. thick, with brick set on edge. Another 4-in. arch may be placed on top of this, if desired. Most of the heat radiated from a furnace passes through the arch, so that the cost of the extra thickness of arch is money well invested. For the arch, fire clay should be used for the joints, and the joints are best made by dipping the brick into the thin clay before setting them in place. If a 4-in. arch is placed over the 8-in. arch, it may be made of brick or brickbats, laid in mortar. The rabble doors are usually about 8 in. high and 14 to 16 in. wide. In front of the door is an iron bar laid across it from projections on the casting, to facilitate the rabbling. The furnace is bound together by 1-in. rods, attached either to cast iron, or railroad iron buck staves.

Long Reverberatory.—The typical hand roasting furnace is the long reverberatory, of which Figs. 3, 4, 5, 6, and 7 show a typical example. It is the type of hand reverberatory almost universally used, and is

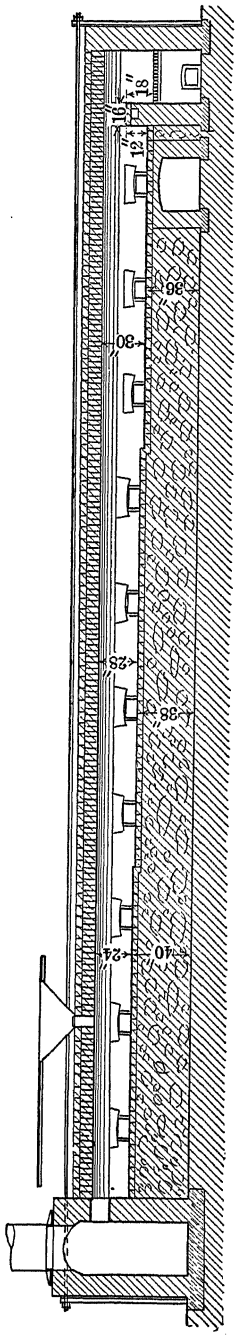


FIG. 3.—Long hand reverberatory. Longitudinal section.

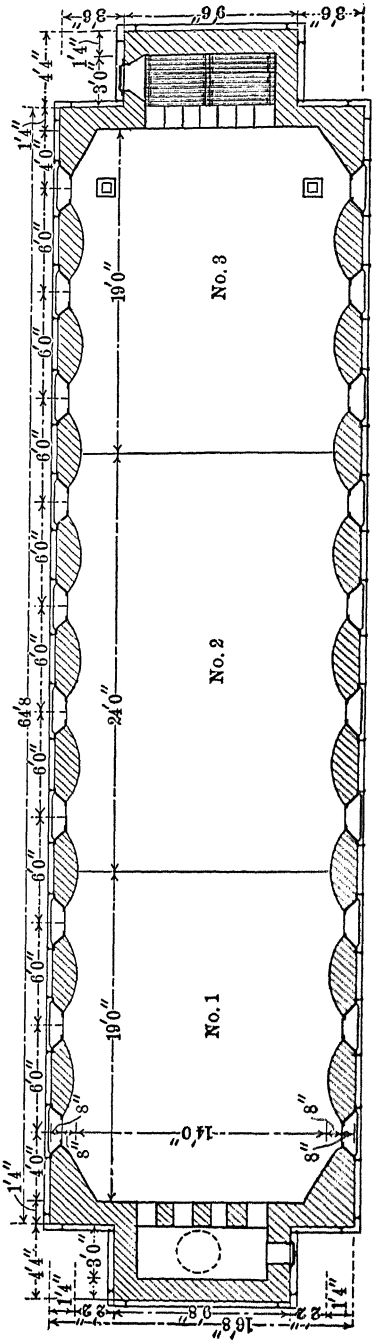


FIG. 4.—Long hand reverberatory. Plan.

essentially the same as those used in smelting works. The length of the furnace is largely governed by the character of the ore to be roasted. If the ore is highly silicious, and contains only a small amount of sulphur, there is no advantage in having the length more than 40 to 50 ft. If the ore is highly pyritic, or consists of ordinary sulphide concentrates, a length of 60 to 75 ft. will be found the most satisfactory. With furnaces longer than 60 to 75 ft., it will be found difficult to ignite the ore at the rear, and unless it is ignited, except for drying and heating, there is no advantage in having the furnace much longer than the zone of ignition. This zone, under any conditions, is considerably shorter in furnaces roasting for the chemical processes than for smelting, because the initial heat at the fire-box, and hearth adjoining, must always be kept below the sintering point of the ore, whereas if the ore is roasted for smelting,

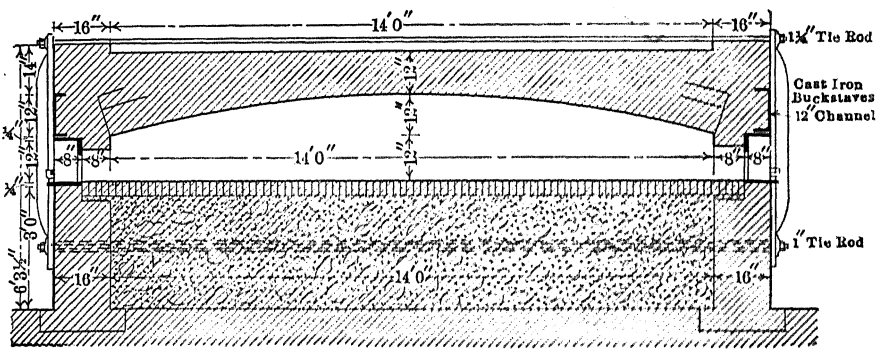


FIG. 5.—Long hand reverberatory. Transverse section.

the sintering is of no particular consequence. It will usually be found advisable, therefore, if increased capacity is desired, to build two furnaces, rather than to attempt to get it by increasing the length of the hearth, or perhaps by the addition of a second fire-box, toward the rear.

The practical width of the furnace is controlled by the convenience of working from both sides. From 14 to 16 ft. has been found by experience to give the best general results. When the width exceeds 16 ft., or a reach of rabbling of about 8 ft., the labor of stirring the ore and advancing it becomes tiresome for the workmen, and hence the quality of the roast is likely to be defective.

The hearth is sometimes made continuous, in one plane, and sometimes with slight breaks of several inches, corresponding in length of hearth to the amount of ore charged into the furnace at one time. The object of the stepped hearth is to enable the roastermen to clearly distinguish the different charges, and keep them separate as they progress through the furnace. As one charge is sufficiently roasted and withdrawn, the next charge is moved forward to the position occupied by the previous

one, and a new charge introduced in the section at the flue end. It is very desirable that mixing of the different charges should not occur. If mixing occurs to any considerable extent, the insufficiently roasted ore will contaminate that which is well roasted and serious difficulty in the chemical treatment will be the result. If the hearth is not stepped, the roastermen work to imaginary lines in the furnace to keep the charges separate. Sometimes, in order to enable the workmen to more easily advance the ore, the hearth is built with a gentle slope from rear to front. The hearth should be built 4 in. thick with brick laid on edge and without mortar. The ordinary quality of pressed brick make an excellent hearth, and these are satisfactory for the arch also.

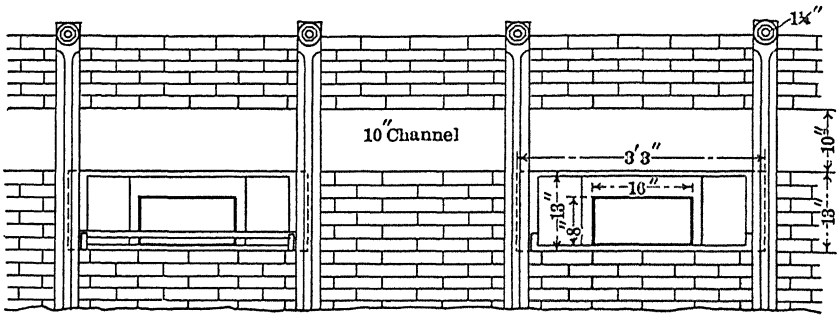


FIG. 6.

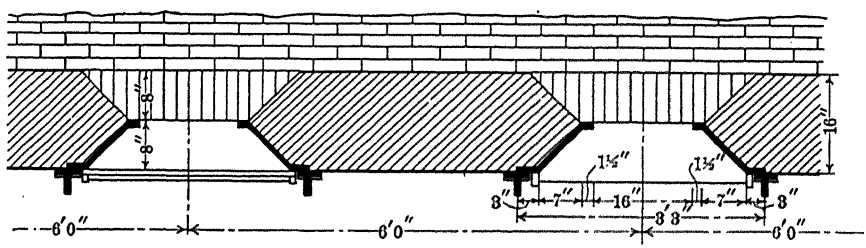


FIG. 7.

FIGS. 6 and 7.—Long hand reverberatory. Details of construction.

The height of the arch above the hearth is dependent largely upon the nature of the ore to be roasted. As a matter of fuel economy, the lower the arch, the more flame and fuel gases will come directly in contact with the ore, but the limit in this direction is governed by the conditions of the furnace atmosphere. When roasting highly silicious ores, the furnace gases will be highly oxidizing under almost any conditions, and the height of the arch above the hearth, in such a case, is therefore limited by other considerations, such as convenience in rabbling. If, however, the ore is high in sulphur, as in roasting pyritic concentrates, the fumes of sulphur dioxide from the ore and carbon dioxide from the

fuel, would tend to make the furnace atmosphere reducing, instead of highly oxidizing, and the object of roasting would be largely defeated. With such ores, the reverberatory arch should be high so as to permit of large volumes of air passing over the ore in order to keep the atmosphere within the furnace as highly oxidizing as possible. From 20 to 36 in. will usually be found to be within the practical limits of the height of the crown of the arch above the hearth. The rise of the arch should not be less than 3/4 to 1 in. for every horizontal foot of width. That is to say, the least rise that an arch 16 ft. wide, should have to be safe, is from 12 to 16 in. Theoretically, a flat arch is the best, but there are practical difficulties in constructing and maintaining a flat arch under the strenuous conditions to which it would be subjected in furnace work. So far as the roasting is concerned, the best results are obtained by having the arch as nearly flat as possible, and the limit in this direction is governed by constructional difficulties. As to the best practical rise for the reverberatory arch, much will depend on the quality of the brick; but the rule given above will be found best under average conditions and conform with the best practice for all types of reverberatories for roasting ores.

The method of constructing the arch is largely a matter of choice. The brick should be set on edge, the 8-in. way. The arch may be built of independent successive rings, as shown in Fig. 8, or be bonded so as to make a continuous whole, as shown in Fig. 9. The method of independent rings has much to commend it. With this construction, every brick

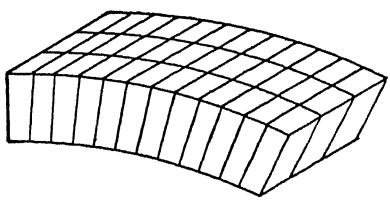


FIG. 8.

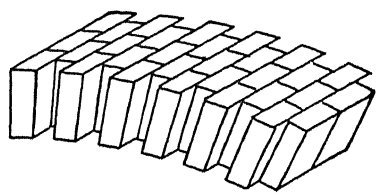


FIG. 9.

FIGS. 8 and 9.—Reverberatory arch construction.

is under full compression, whereas in the bonded arch, if the brick or joints are not of equal size, it is not possible to have them all under the same compression, so that there is danger of the thinner ones dropping out.

The reverberatory arch is usually built of ordinary straight brick, with the difference in the thickness of the joint between the intrados and extrados made up with clay. It is better, however, to build the arch of straight brick and occasionally insert a row of wedge brick. In this way the joints can all be kept of even thickness and the arch will have greater stability. It will not be necessary to carry the fire brick in the arch more than 10 or 20 ft. beyond the fire-box, in the roasting chamber.

The remainder of the arch, as also the side walls, may be built of common brick.

The side and end walls should not be less than 16 in. thick, or two courses of brick laid the 8-in. way. A little extra cost in thick walls and reverberatory arch, will be more than compensated for in the saving of fuel and comfort to the workmen.

The foundations are best and cheapest made of concrete. By putting up the necessary side boards, and leveling the top edges, the foundation can be quickly and cheaply laid in the best possible condition for the superstructure. The concrete may be brought up to within a foot of the hearth level, and this also will be found cheaper than brickwork and be just as good. Brickwork, in mining districts, and especially in isolated camps, is expensive, since all the material has to be hauled on the ground, and brick-layers command high wages. With concrete, only the cement, which is a small proportion of the whole, has to be supplied from without, since rock and sand are usually available and common labor all that is required.

The lower tie-rods should not be built in solid, but ducts should be provided so that they can be removed or inserted at will, should the rods at any time become disabled. Worn out iron piping, or common earthenware pipes, are the best for this purpose, although ducts made of brick will answer about as well.

The space between the walls, below the hearth, may be filled with rock and earth or loam. It should be well tamped, so that there will be no danger of the hearth settling when the furnace is in operation.

The rabble door frames should be set flush with the hearth and also with the exterior walls. The buckstaves will then lap the joint between the exterior brickwork and the iron castings, and catch the face of the channel which takes the thrust of the arch. The rabble door castings are in this way securely fastened without bolts. Instead of the channel as shown in the drawings, cast iron beams in the form of T's may be used to support the arch, and which alternate with the rabble door castings. The buckstaves may be made of old railroad rails, I-beams, cast T-irons or two small channels secured together, back to back, with a separator to permit the tie-rods to go between them. It is well to have the tie-rods abundantly heavy to take the enormous horizontal thrust of the arch. For the ordinary span of from 12 to 16 ft., 1 1/4-in. rods have been found satisfactory. For the longitudinal rods 3/4-in. diameter will be large enough.

The number of working doors should be sufficiently numerous to permit of easy rabbling. A distance of about 6 ft., from center to center, is satisfactory. When the doors are too far apart, rabbling of the ore in the intermediate spaces becomes difficult, and may be neglected. Figs. 6 and 7 show the details of the working doors and the method of setting

them. The details may vary somewhat according to the material most convenient, and upon local conditions. Each door casting has attached to it lugs which receive an iron bar about an inch square upon which the rabble may slide while the ore is being rabbled. These bars are removable, and sometimes it is more convenient to work without them. The door castings have flanges on the sides so that they can be secured in place by the buckstaves. Each door casting weighs about 150 lb.

When odd shaped bricks are used, it will be found cheaper and better to have them especially made for the purpose if they cannot be obtained in standard shapes. The cutting, and consequent breaking, of a large number of brick will be more expensive than the extra cost of special forms, and the work will not be as good. Usually the manufacturers of fire brick have special shapes enough to fill any want.

All brickwork about a furnace should be "shoved" and well grouted, especially that part of the work which forms the skewback of the reverberatory arch. The spandrels of the arch may be filled in with brickbats and mortar. The filling in of the spandrels will make the arch stronger and also enable the furnace to better retain the heat.

After the furnace is finished, the buckstaves and tie-rods should be put in place. The rods should be made reasonably tight, so that they will vibrate when struck. It is best to take up any looseness in the arch before its weight is taken off the centers. The centers may then be removed, either before firing, or they may be burned out afterward, whichever is the most convenient and economical. The furnace should be allowed to stand as long as possible before firing. When the fire is started the furnace should be heated quite gradually for at least 24 hours, after which there will be no harm in bringing it up to heat. It should be fired long enough to get the hearth quite hot before charging the ore, since a cold hearth greatly retards the roasting.

The furnace should be provided with several rabbles, 4 in. by 8 in., and 12 to 14 ft. long, and several paddles 8 in. by 12 in., 14 ft. long. The handles are best made of strong wrought iron pipe to which the rabble and paddle blades are fastened, by welding.

The stack of the furnace may be built of brick, iron, or re-enforced concrete. For single furnaces an iron stack will usually be found the most economical. The stack for a furnace as shown in Figs. 3, 4, and 5, should be about 30 in. in diameter and from 60 to 75 ft. high. The stack, or the flue leading to the stack, should be provided with a damper. The position of the stack in reference to the furnace, is largely a matter of convenience and local conditions. If the works have several furnaces, they may all connect with a common stack. If there is only one furnace, and no dust chamber is desired, the arrangement of the stack as shown in Figs. 3 and 4 will be as satisfactory as any. Provision should be made for a car track to bring the ore to the hopper over the rear of the furnace.

Hand reverberatories should not make more than 3/4 to 1 1/2 per cent. dust. Whether this dust is worth recovering by building a large dust chamber will depend largely on the value of the ore. Small dust chambers are not very effective. It will ordinarily be found that the recovery of the dust is a matter worth careful consideration.

The cost of building a long reverberatory, as described and shown, will be between $3000 and $4000. It will take about 50,000 common brick, 8000 fire brick, and 20,000 lb. of iron. If concrete is largely used, a great saving may be effected in the number of brick, and a saving also in the cost of the furnace.

Method of Operating a Long Hand Reverberatory.—When the furnace is hot, the ore, which may be assumed to be pyritic concentrates, is charged from a car into the hopper, and into the furnace, in the section nearest the flue, or at the rear. It is then spread out evenly over this section of the hearth. The weight of the charge, for the best work, should not exceed 10 to 15 lb. per square foot of hearth area; 10 lb. is better than 15 lb. if the ore contains very much sulphur. In any event, there is no advantage in using a deep bed of ore, for what is gained in the amount of ore charged, is lost by a correspondingly increased time of roasting. The depth of the charge will usually be from 2 to 3 in.

The working doors are all closed until the sulphur is well ignited. The moisture is first driven off, after which the ore will soon become slightly incandescent and the sulphur begin to burn with a blue flame. This is one of the most delicate stages of the roasting, and should be done at the lowest permissible temperature and in the presence of a maximum amount of air. The charge should be rabbled energetically, and with the intervals between the rabbling as short as possible. At this stage the ore will be very unstable and is likely to run somewhat like a liquid. If the rabbling is neglected, or if the temperature of the furnace is too high, partial fusing or matting is likely to occur, which forms lumps that are difficult to eliminate; and if not eliminated, will result in improperly and insufficiently roasted ore. Such ore will be highly detrimental in the subsequent chemical treatment. The excess of air required during this stage of the roasting may be obtained by keeping the working doors open, and by free admission of air through the bridge wall. The air should be introduced as much as possible through the bridge, since this will tend to keep the charge nearest the fire from becoming too hot, by interposing a layer of cooler air between the ore and the flame, and give a highly oxidizing atmosphere at the surface of the ore where it is most desired.

When the sulphur flame has abated, which will be in about 8 hours after charging, the ore is moved forward into section No. 2, and a new charge introduced into section No. 1. The ore on section No. 2 is spread out over a large area to give it as much surface as possible. There is still much sulphur in the ore, and most of the oxidation takes place in the

middle section. The ore being brought closer to the fire, is brought to a dull red heat. During this stage the ore swells somewhat, and becomes more or less inert. As the sulphur is eliminated, the ore has no power of generating heat within itself and hence the fire is urged, to keep the ore at the desired temperature. The rabbling in this section need not be as frequent as in section No. 1; a thorough stirring every 15 or 20 minutes will suffice. The ore should be uniform throughout, and as it is turned over, the newly exposed incandescent surface should quickly turn dark and not show any live sparks of burning sulphur.

The charge, after reaching this stage, which will usually be about 16 hours after it has been put into the furnace, is transferred to section No. 3; the ore in No. 1 is advanced to section No. 2, and a new charge introduced into section No. 1. There is now no danger of lumps forming in section No. 3, and the temperature may be raised somewhat, but must never approach the sintering point. The temperature permissible in this section is the controlling factor in firing the furnace. The firing should always be done with a view of throwing as much heat and flame as possible to the rear of the furnace without danger of sintering the ore on the finishing section. In this section, the roasting will largely consist of decomposing the soluble sulphates, and while this is going on the odor of sulphur dioxide can be detected when a sample of the incandescent ore is removed for inspection. As the ore becomes more nearly completely roasted, it becomes more coherent, and remains as placed by the rabble.

"Sweet" or "Dead" roasting are more or less indefinite terms, used to denote the condition of the ore when all the sulphur has been eliminated. But as the elimination of all the sulphur is practically impossible, and as the approximation thereto is a very indefinite matter varying with the different ores, it may be taken to mean ore sufficiently roasted to give the best results in the subsequent chemical treatment.

After the ore has remained on the finishing section for about 7 hours, the roasting is completed. It is then withdrawn through the holes in the hearth, near the last door, into a pit, or into a car and taken to the cooling floor. The charge in section No. 2 is then moved forward to No. 3, and the charge in section No. 1 moved forward to No. 2, while a new charge is introduced into section No. 1. In this way a charge is withdrawn and a new one added every day, so that there are always three separate charges in the furnace, and each charge remains in the furnace almost 24 hours.

The fuel used in roasting should be either wood or long flame coal. Oil gives better results than either wood or coal, but is not usually available. It is best, in order to get a long flame, with almost any coal, to fire the furnace fire-box more or less as a gas producer. This is easily arranged by keeping a deep bed of ash and fuel on the grates, and introducing steam and air through the closed ash pit. Much of the air needed

to completely consume the fuel gases may be introduced through the bridge and some through the working doors. The draft is regulated by the damper in the flue or stack, and by opening and closing the working doors. The time of roasting depends largely on the ore, but somewhat also on the amount of rabbling. Roasting, as already stated, is essentially an oxidizing process, so that any operation, such as continuous and energetic rabbling, which will expose the greatest amount of ore to the highly oxidizing furnace atmosphere, will materially reduce the time of operation.

It is customary when roasting pyritic gold concentrates, or ore containing lime, or silver and copper in appreciable quantities, to add a small amount of salt, usually just before drawing the charge. The amount of salt may vary from 0.5 to 5 per cent. If the ore is not sensitive to volatilization, the salt may be added to the ore as it is advanced from the middle to the finishing section and thus become thoroughly incorporated with it. Usually, however, the salt is added about 30 minutes before the charge is withdrawn, and thoroughly mixed with the ore. Chloridization, under proper conditions, takes place rather quickly, and as explained under "Chloridizing Roasting" air is not essential to the chloridization. The salt may therefore be added a short time before discharging the ore, and by permitting the ore to cool slowly after it is discharged, the necessary degree of chloridization can well be realized without any appreciable loss by volatilization. This gives the ore a thorough oxidizing roast before chloridization, and the sulphur is never so thoroughly eliminated but that there are always enough sulphates left to sufficiently chloridize the silver and small amounts of copper.

After the salt is added, the ore begins to fume, increase in bulk, and has a "woolly" appearance. After the salt is added the temperature should be kept low—not over a dull red heat. Much of the gold is chloridized as well as the silver; careful tests have shown it to be from 10 to 20 per cent. of the gold contained in the ore.

If the ore contains galena, great care must be exercised in the first stages of the roasting to keep the charge at the lowest practicable temperature, as the lead sulphide fuses at a very low heat, and agglomeration in the early stages of the roasting will make the subsequent work more difficult.

Furnaces having considerable of a drop between the different sections of the hearth have been recomended and built, but have not come into general use. The cause of this is evident. While theoretically the showering of ore through this drop, as in a shaft furnace, appears good, it is evident that the draft in the furnace will whip the dust along with it and cause excessive loss in that way. The great dust loss is not compensated for by the small gain in the time of roasting.

Most furnaces, like the one illustrated in Figs. 3, 4, and 5, are de-

signed to take a charge of from 3 to 3 1/2 tons on a section. It is usual, however, instead of charging and withdrawing this amount of ore all at once, to still furthur subdivide it so that each shift of eight hours will charge and withdraw one third of this amount or from 2000 to 2400 lb. The advantage of this is that the quality and quantity of the roasted material can be checked up for the different shifts, and the furnace can be worked with greater regularity, than when so much ore is charged and withdrawn at the same time.

One man on a shift, working three shifts, will roast from 3 to 3 1/2 tons of pyritic concentrates a day. Each shift will draw a charge of from 2000 to 2400 lb. and introduce one. The amount of fuel used is 1/2 cord of wood per ton of concentrates.

The following tabulated statement gives the essential facts of roasting pyritic concentrates in California:[1]

ANALYSES OF CONCENTRATES

	Eureka and Idaho mines, Grass Valley	Washington mine, Mariposa County	Black Bear mine, Klamath County
Copper	0.85	0.00	0.00
Lead	0.78	1.50	0.00
Gold	0.02743	0.00914	0.0137
Silver	0.0068	0.0035	0.003
Zinc	0.00	1.34	0.00
Iron	40.65	30.85	42.05
Arsenic	trace	0.00	31.25
Sulphur	32.80	31.33	25.10
Silica	12.64	33.30	10.35
Alumina	0.10	0.00	0.85
Magnesia	3.50	0.00	0.85
Oxygen and loss by difference	8.65	1.67	0.38

These analyses give a very good idea of the composition of California pyritic concentrates, which have been treated for many years by roasting and chlorination. The size of some of the furnaces, the time of working on a shift, and the quantity of ore treated, is given in the following table:

Name of works	Size of furnace	Time of working (shift)	Quantity of ore in 24 hours
Heywood's	60×12	8 hours	3 tons
Zeile	75×12	8 hours	3 tons
Amador	80×12	8 hours	4 1/2 tons
Plymoth	50×12	8 hours	3 tons
Maltman's	60×12	8 hours	2 1/2 tons
Merrifield's	70×10	12 hours	3 tons

[1] Eggleston, "Met. Silver, Gold, Mer."

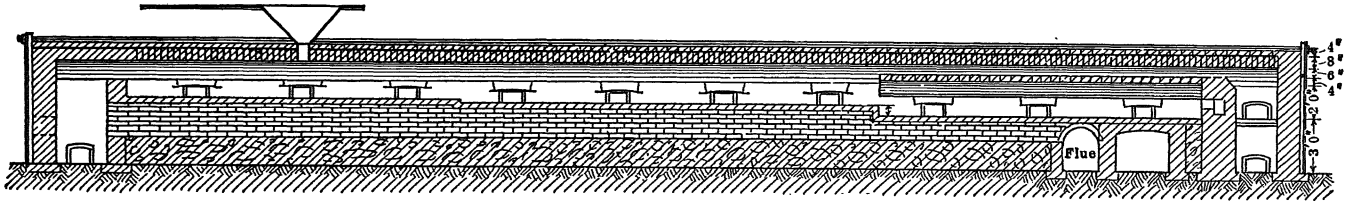


FIG. 10.—Modified long hand reverberatory. Longitudinal section.

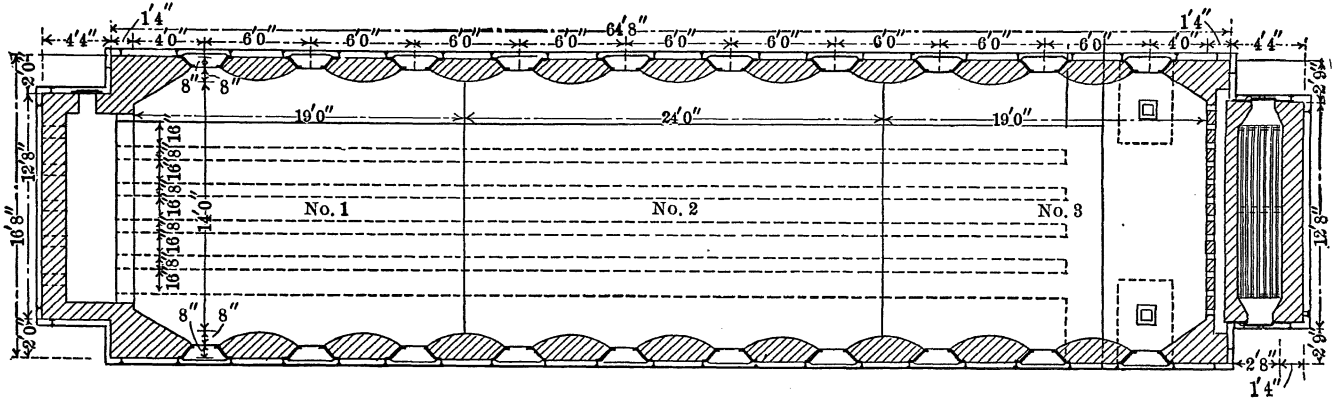


FIG. 11.—Modified long hand reverberatory. Plan.

The hearth of these furnaces lasted from four to six years.

Cost of Roasting in Long Reverberatories.—The cost of roasting in long reverberatories is quite large. For pyritic concentrates, which is about the only material roasted in these furnaces, it is about $4.25 per ton, distributed as follows:

Roasterman, 1 shift, roasting one ton,	$2.50
Fuel, 1/2 cord of wood, for one shift,	1.50
Other expenses,	0.25
	$4.25

The cost of roasting silicious ore, low in sulphur, is very much less. Such ore can be roasted about as rapidly as it can be worked through the furnace.

In California[1] at one of the mills where oil was substituted for wood, it was found that the capacity of the furnace was increased from 4 tons to 6 tons per day. The furnace was 14 ft. wide and 75 ft. long. Bakersfield crude oil, of 14 to 16° gravity, was used. In roasting 2647 1/4 tons of pyritic concentrates, 1290 barrels of Bakersfield crude oil was used which cost, delivered, $1917.63 or 48/100 barrel per ton of ore, costing 72 cents. There was also used 66.76 tons of coal to generate steam for pumping, heating, and atomizing the oil, which cost delivered, $867.84, or 35 cents per ton of ore treated; making a total cost of fuel for roasting, of $2785.47 or $1.05 per ton.

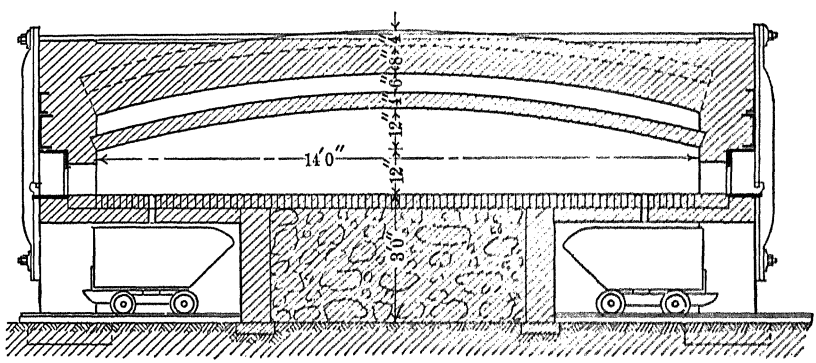


FIG. 12.—Modified long hand reverberatory. Transverse section.

Modified Long Reverberatories.—An important modification of the long reverberatory, especially for copper roasting, is shown in Figs. 10, 11, and 12. Fig. 10 shows a longitudinal section; Fig. 11 the plan, and Fig. 12 a transverse section through the front of the furnace at the protecting arch and discharge openings in the hearth.

One of the difficulties in hand reverberatories in roasting ore for the hydrometallurgical processes is the liability to fuse the ore near the fire

[1]E. C. Vorhies, *Scientific and Mining Press*, March 26, 1904.

end, when the fire is urged sufficiently to ignite the charge at the rear. In chloridizing roasting a similar difficulty presents itself. In order to eliminate the sulphur sufficiently in hearth section No. 2, by oxidizing roasting, a temperature nearly as high as the ore will stand without fusing is desirable to expedite the process as much as possible. To accomplish this the ore in section No. 3 may become unduly heated, even if it does

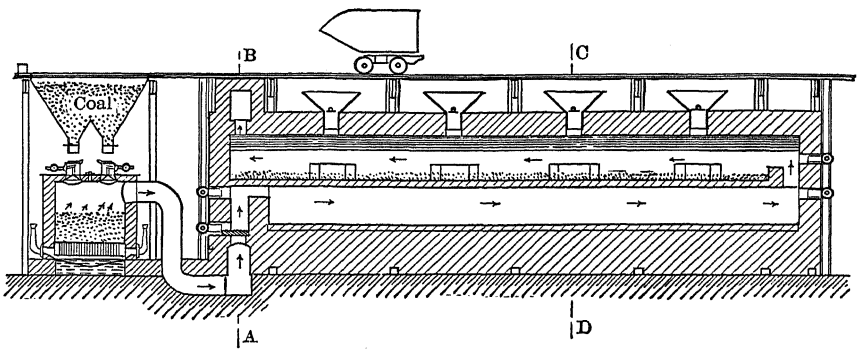


FIG. 13.—Modified hand reverberatory. Longitudinal section.

not approach the sintering point. The temperature for chloridizing roasting should be the lowest at which the reactions take place, and this condition conflicts with that required for efficient roasting in the middle and rear end of the furnace.

To overcome these difficulties, a protecting arch is thrown over section No. 3, as shown in Figs. 10 and 12, which shields the ore from the

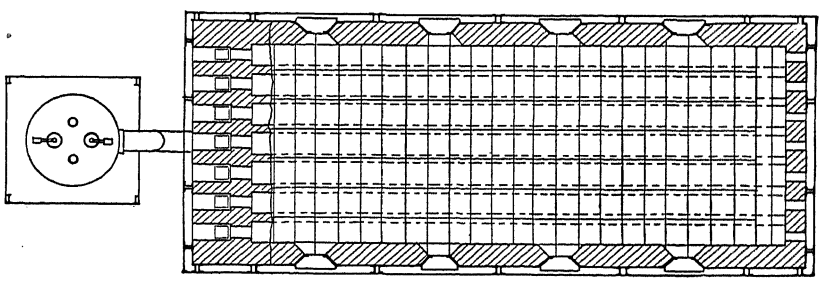


FIG. 14.—Modified hand reverberatory. Plan.

direct action of the heat and flame. In this way the ore in the middle section may be kept the hottest, and that in the rear section may readily be ignited. The flame and heat from the fire-box pass through the space between the protecting arch and the reverberatory arch, so that the ore in the finishing section is heated only indirectly, as in a muffle. The protecting arch should be as thin as possible, consistent with good construction.

In the chloridizing roasting of copper ores, this modified furnace has been used in preference to the ordinary long reverberatory. It can readily be seen, that for chloridizing work especially, this modification of the long reverberatory offers many advantages. The furnace may be still further modified by returning the flues under the hearth, and thus heat the ore from below. In a long furnace this is a doubtful utility. Much will depend on the temperature of the furnace gases.

Figs. 13, 14, 15, and 16 show a modification of the hand reverberatory, at one time used in Europe for roasting copper ores.

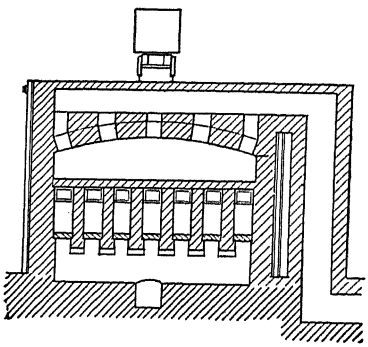


FIG. 15.

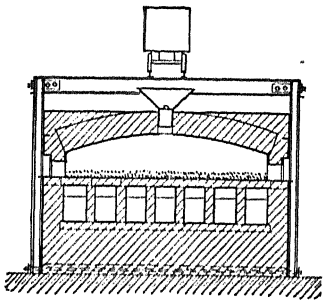


FIG. 16.

FIGS. 15 and 16.—Modified hand reverberatory. Transverse sections through A–B and C–D (Fig. 13).

Mechanical Reverberatories.—Practically all the roasting at the present time, in preparing ores for treatment by wet methods, is done in mechanically operated reverberatories. With the exception of the rabbling mechanism, these furnaces are not essentially different from the hand reverberatories.

The mechanical reverberatories differ mostly from each other in the rabbling mechanism. They may have one long roasting hearth, or several hearths superimposed above one another.

The single hearth furnaces have the advantage of making less dust than the multiple hearth roasters; while, on the other hand, the multiple hearth furnaces are more compact and better conserve the heat.

In roasting ores for chemical treatment, where a more or less complete roast is necessary, single hearth furnaces have usually been preferred, largely on account of the low dust loss. Multiple hearth furnaces have also been largely used, and their use is becoming more general.

In roasting pyritic concentrates or heavy sulphide ore down to 6 or 8 per cent. sulphur, which may be done without fuel, the multiple hearth roasters have found more favor than the single hearth furnaces. Recently the multiple hearth furnaces have been modified by the

addition of fire-boxes for the different hearths, so that the sulphur can be eliminated quite as completely as in single hearth furnaces.

The advantages of the multiple hearth furnace is that the heat from the ore and fire-boxes in the lower hearths, heats the bottom of the upper hearths, and this heat is very effectively applied. The disadvantage is that when ores are roasted with external fuel, the volume of air necessary for the combustion of both fuel and the sulphur in the ore is very large, and the ore dropping from one hearth to another against a strong current of ascending gases, makes considerable dust, much of which is lost unless efficient means is provided for its recovery. This difficulty may to some extent be obviated by providing separate flues for the ore and gases between the hearths, or by exhausting the gases from one or more of the intermediate hearths as well as from the upper hearth.

In roasting heavy sulphide material down to 6 or 8 per cent. sulphur, fuel is not ordinarily necessary, hence the volume of air and gases going through the furnace is comparatively small and its rate of passage comparatively slow, hence the dust loss in dropping the ore from one hearth to the next need not be serious or excessive. In roasting ores for treatment by wet methods, the furnace operates under much higher temperatures than in roasting for smelting, where the sulphur most difficult to eliminate, remains in the ore. Usually furnaces, for sweet roasting, work under a temperature of from 1200 to 1700° F. The ore itself may not be at these temperatures, but the reverberatory chamber in which the rabbling mechanism operates, is. The temperature of the reverberatory chamber, at the fire-boxes may even exceed 1700° F. in regular roasting work, and for that reason, if anything goes wrong with the rabbling mechanism, it is necessary to at once cool the furnace or the top layer of ore would take the same temperature as the reverberatory gases, become sintered, and be unfit for extraction by hydrometallurgical processes.

The problem, therefore, in mechanically roasting ores, has been to provide a rabbling mechanism which will work in grit and dust and at a temperature varying from 1200 to 1700° F., without serious delays or excessive repairs. The different mechanical roasting furnaces are based fundamentally, on the method of overcoming these difficulties.

O'Harra dragged the rabbles through a straight line reverberatory by means of a chain and track within the reverberatory chamber. Brown conceived the idea of placing a supplemental chamber on both sides of the reverberatory hearth, containing the tracks on which run the rabble trucks, shielded more or less from the direct heat and dust of the reverberatory chamber. Holthoff-Wethey placed the trucks entirely outside of the furnace and devised a slot arrangement which opened and closed automatically as the rabble moved along. Pearce supported the rabbling mechanism by a column in the central open space of two concen-

tric walls forming the reverberatory chamber, the inside wall of which is slotted and the reverberatory arch supported from above. Edwards and Merton have a longitudinal series of rabbles of a diameter corresponding to the width of the hearth, projecting through the reverberatory arch, and as the ore is advanced by one of these rabbles, it is delivered to the next, and so on until it issues from the furnace. The multiple hearth furnaces are mostly based on the support and protection of the central column carrying the rabbles for the different hearths and the arrangement for cooling and replacing either the rabble arms or the blades.

Any single hearth reverberatory may be constructed with multiple hearths, but when so modified, it is questionable whether they are as efficient and present the same advantages as the regular circular multiple hearth furnace of the McDougall type.

For furnaces where the rabbles are alternately within and without the roasting chamber, as in the O'Harra, Brown, and Holthoff-Wethey, no special cooling provision is necessary, since the rabbles never get dangerously hot, and never, except in case of accident, do the rabbles have the same temperature as the reverberatory chamber. When the rabbling mechanism remains in the furnace indefinitely, as in the Pearce, Edwards, Merton, McDougall, Herreshoff, and Wedge, water cooling is necessary or desirable. Air cooling, for sweet roasting, has not given satisfactory results.

There is no great difference in the cost of installation of the various mechanical reverberatories, and on the same ore, for a thorough roast for wet processes, there is no great difference in the cost of operation.

In roasting Cripple Creek ore, for example, there are three 100-ton Pearce roasters in one reduction works; six 100-ton Holthoff-Wethey at another, and eight 100-ton Edwards at still another, all in successful and satisfactory operation, roasting in all about 1500 tons of ore daily and having a precious metal content of approximately $30,000.

Cost of Mechanical Reverberatories.—The average cost of a good mechanical reverberatory is about $15 per square foot of hearth area for the smaller sizes, and about $12 per square foot of hearth area for the larger sizes, installed, ready to operate, but not housed.

Fuel Required in Roasting.—The fuel consumption in wood or coal will usually be from 10 to 15 per cent. of the weight of the ore roasted, and will be more or less independent of the original sulphur content. For ore low in sulphur, considerable fuel is required to bring it to the roasting temperature and to maintain it at that temperature. For ore high in sulphur, the sulphur itself develops considerable heat, so that extreme firing is not necessary except to remove the last few per cent. of sulphur. On sulphide concentrates or heavy sulphide ore, the sulphur content in the roasted material may be reduced to 6 or 8 per cent. without any fuel, and

to 4 and 6 per cent. with only one fire-box at the finishing end of the furnace. It is in the elimination of the last few per cent. of the sulphur that most of the fuel is consumed. But if the fuel consumption is more or less independent of the sulphur content of the ore, the capacity of the furnace is more or less proportion to the contained sulphur.

Hearth Area Required in Roasting Various Ores.—The capacity of a roasting furnace is dependent on the amount of sulphur in the raw ore, and on the amount of sulphur to be eliminated. For roasting ores suitable for the hydrometallurgical processes, the hearth areas required are approximately as follows:

For silicious ore containing from 1.5 to 3.5 per cent. sulphur will require from 10 to 15 sq. ft. of hearth area per ton of ore roasted per day; ores containing from 10 to 15 per cent. will require a hearth area of from 25 to 30 sq. ft., and pyritic concentrates which carry from 35 to 45 per cent. sulphur will require from 40 to 50 sq. ft.

Pyritic concentrates and heavy sulphide ores, carrying 28 per cent. or more of sulphur are self roasting down to 6 or 8 per cent. After that fuel has to be used to complete the roast, to make the ore suitable for a solvent process.

The Brown Furnace.—The latest and most approved type of Brown furnace is shown in Figs. 17 and 18, which is a straight line reverberatory, in which the ore is stirred and advanced by rabbles mounted on trucks attached to endless chains, one on each side of the furnace, moving in a supplemental chamber. Brown was the first to work out a successful method of protecting the rabbling mechanism in a straight line furnace from the heat and dust of the reverberatory chamber.

The Brown furnace has had various modifications, but in its most approved form it is a single hearth reverberatory, with supplemental chambers on each side of the roasting chamber, to protect the rabbling mechanism. The supplemental chambers are formed as shown in Fig. 18 by a tile projecting up from the hearth, above the level of the ore, and a corresponding tile, forming part of the reverberatory arch, projecting down from above. This construction forms a supplemental chamber and leaves a slot between the roasting and supplemental chambers just large enough for the rabble arm to pass through. The rabble arm, at the slot, is usually made rather wide and about an inch thick so that the slot may be as narrow as possible.

The rabbles, extending from one side of the furnace to the other, are mounted on trucks on each side, and these trucks run on tracks in the supplemental chambers. The trucks are attached to endless chains which move about sprocket wheels at each end of the furnace. One pair of these sprockets is driven by means of spurs and gears, which in turn are actuated by a counter shaft driven by belt and pulley.

The rabbles in passing through the furnace stir and advance the

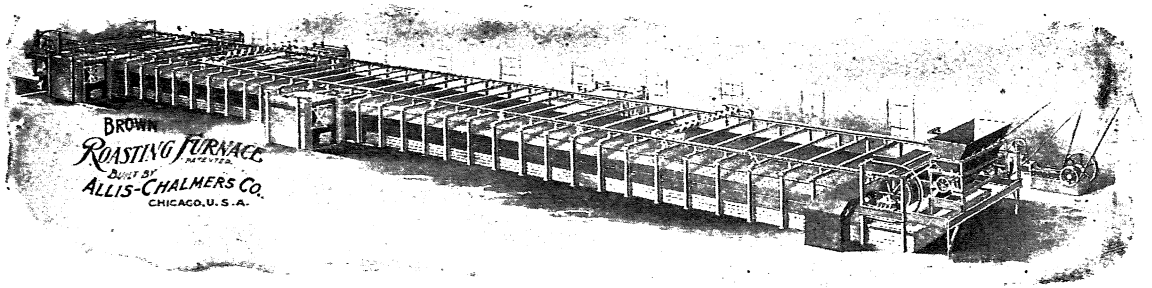


FIG. 17.—Brown furnace. Perspective view.

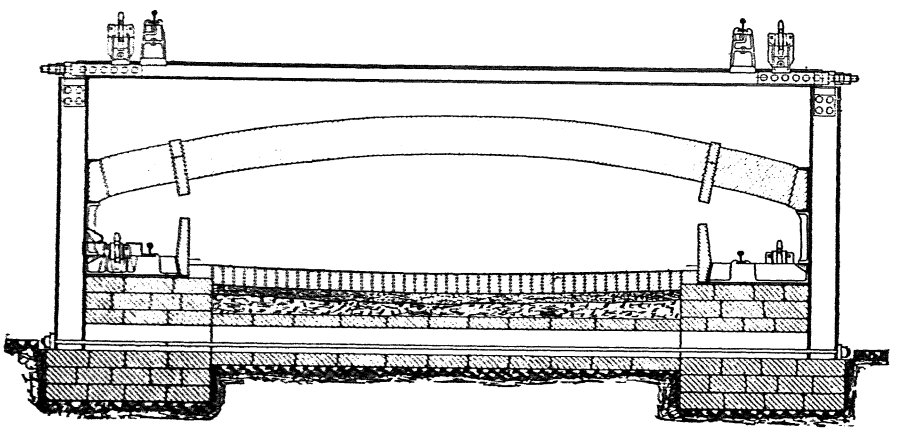


FIG. 18.—Brown furnace. Transverse section.

ore, and issue quite hot; then elevated by the sprocket wheels at the other end of the furnace to a track above, and returned to the feed end where they are again lowered by the driving sprockets and enter the reverberatory chamber to again complete the circuit. While returning, outside of the reverberatory chamber, the rabbles are cooled enough so that no special cooling device is necessary. As each rabble enters the furnace it takes with it from the feed bin the proportionate amount of ore required to make the daily output. This may be regulated by the feeding device or by the depth of raw ore in the path of the rabble as it enters the furnace.

Counterweighted sheet iron doors at both ends of the furnace, hinged at the top, keep out the cold air; they remain closed except when lifted by the rabbles in passing in and out. When the doors are opened, even momentarily, a strong inward draft is likely to set in; to avoid this, two doors are sometimes inserted at each end a short distance apart so as to form a neutral air chamber; one door being always closed while the other is opened by the moving rabble.

The skewbacks of the arch are steel channels supported by the buckstaves and short cast iron columns, the spaces between the columns being 3 ft. 6 in. long by 12 in. high. These openings extend the entire length of the hearth; they are closed by sheet-iron doors, lined with asbestos. This construction permits of ready access to the hearth at any point for repairs and observation.

From the ground to the hearth the furnace may conveniently be built of concrete or uncut stone and the remainder of the furnace constructed of brick. The furnace is bound together by steel I-beams which also carry the tracks on the top of the furnace.

The furnace is regularly made with a roasting hearth 10 ft. wide, and in lengths varying from 60 to 200 ft., or even longer. The roasted ore may be elevated to the top of the furnace to a sheet iron hearth supported by the steel I-beams, and there cooled and advanced by the returning rabbles, or the roasting hearth may be somewhat extended and used as a cooler, unless it is preferred to cool the ore independently of the furnace mechanism.

The frequency of stirring the ore may be regulated both by the speed of travel and the number of rabbles on the moving chains.

The size of the sprockets is governed by the vertical distance between the roasting and cooling hearths. In driving the chain mechanism both spockets at the drive end are made tight to the shaft, while at the other end one of the sprockets is tight to the shaft and the other loose, so that any uneven strain in the chain is self adjusting and prevents the chain from riding the sprockets and being thrown off.

The material for a standard straight line Brown furnace 10 ft. wide by 140 ft. long, actually erected, was as follows:

Weight of ironwork, 63,000 lb.
Weight of tiles, 35,000 lb.

The *Brick, etc.*, required for this furnace are as follows:

For Hearth

46,200 common red brick,
420 partition tiles,
14 cu. yd. of sand,
16,800 lb. of ground fire clay,
11 barrels of cement,
126 cu. yd. of stone for concrete work.
Mortar for Hearth; 5 cu. yd. of sand and 42 bu. of lime.

For Arch

1260 common red brick
1344 skewback brick.

For Five Fire-Boxes (one double and three single fire-boxes)

15,000 common red brick,
10,000 common fire brick,
509 arch tiles 12 in. long,
115 arch tiles 6 in. long,
10 fire-door tiles.
For Mortar; 2 1/2 cu.yd. of sand and 25 bu. of lime.

Power.—The Power required to drive the furnace mechanism, etc. was supplied by a 9 in. by 12 in. slide valve engine, which is rated at about 25 h. p. but the engine was never taxed to its capacity at any time.

Grate Area.—The total area of the grates in the five fire-boxes is about 63 sq. ft.

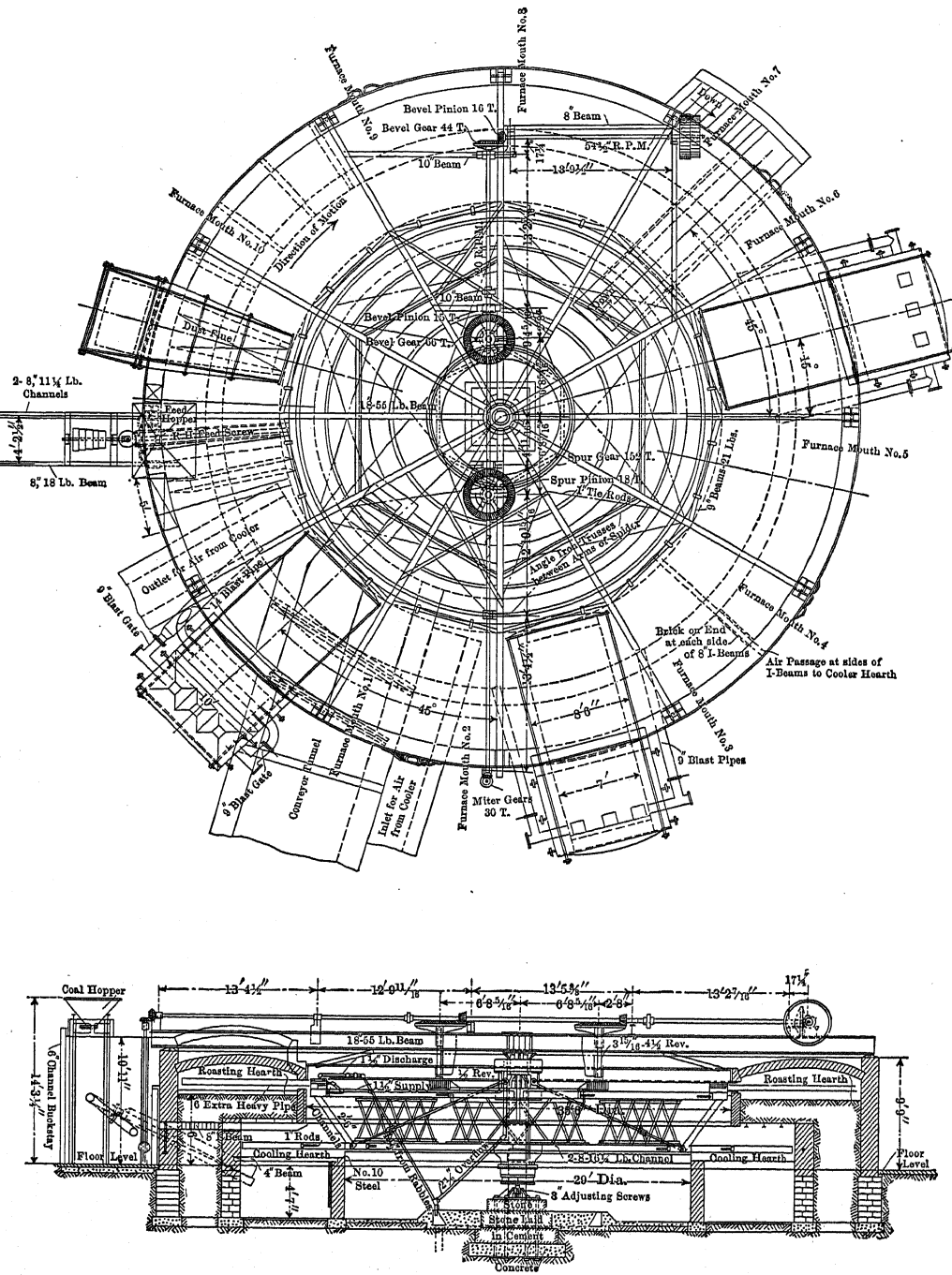
In supplying the above material 5 per cent. extra was allowed for tile and skewback brick, and 10 per cent, on the remainder of the items.

H. O. Hofman[1] gives the following data on roasting with Brown furnaces with a hearth 8 ft. wide and 135 ft. long:

Silicious ore with pyrite, crushed to 30 mesh and containing 2.5 per cent. sulphur was roasted at the rate of 95 tons per 24 hours with 6 cords of wood; sulphur in roasted ore, 0.3 per cent.; roasted ore per square foot of hearth area, 131 lb.; ratio of hearth to grate area 32 to 1; 15.83 tons of ore were roasted per cord of wood.

Silicious ore with pyrite crushed to 20 mesh, containing 2.3 per cent. sulphur, was roasted at the rate of 65 tons in 24 hours, with 6 cords of wood; sulphur in roasted ore, 0.5 per cent.; ore roasted per square foot of hearth area, 90 lb.; ratio of hearth to grate area, 32 to 1; 10.85 tons of ore were roasted per cord of wood.

[1] "The Metallurgy of Lead," p. 185.



FIGS. 19 and 20.—Plan and section, Pearce furnace.
With combined roasting and cooling hearth.

Silicious ore with pyrite crushed to 16 mesh and containing 2.5 per cent. sulphur was roasted at the rate of 50 tons per 24 hours with 4.5 tons of refuse slack coal; sulphur in roasted ore 0.5 per cent.; ore roasted per square foot of hearth area, 77.0 lb.; ratio of hearth to grate area 28.66 to 1; per cent. of fuel on ore, 8.5.

Copper matte, crushed to 40 mesh and containing 20 per cent. sulphur and 40 per cent. copper, and 15 per cent. lead, was roasted at the rate of 20 tons per day; sulphur in roasted ore, 6.0 per cent. the aim of the roast being to peroxidize the iron and convert as much as possible of the copper into soluble sulphate; ore roasted per square foot of hearth area, 38 lb.; ratio of hearth grate area, 35 to 1; coal consumed 3.25 tons· per cent. of fuel on ore, 16.

The Pearce Furnace.—The Pearce furnace, Figs. 19 and 20, is of the circular hearth type. The hearth is formed by two concentric walls, usually about 10 ft. apart. The operating mechanism is at the center, from which the rabble arms radiate.

The ore is fed into the furnace from a hopper, to a tapering screw located beneath the hearth, which distributes and raises the ore across its width, so that each rabble blade takes its proportionate share as it comes along. The rabble blades are attached to the horizontal pipe rabble arms, which in turn, are attached to a rigid iron framework radiating from a hollow hub, at the center. The hub revolves on ball bearings, around a stationary cast iron column.

The rabble arm is made of two concentric pipes, the smaller one being fitted into the larger, and having holes at the end. These rabbles are continuously water cooled by a gravity system. The water from the main is run into a trough located above the level of the rabbles and revolving with the rabbling mechanism. It then flows by gravity into the inner concentric pipe of the rabble arm to the further end, where it is delivered to the rabble pipe, which is exposed to the heat of the furnace, and flows back again to the other end of the rabble arm, from whence it is exhausted into a stationary circular trough about the hub, near the floor. A complete and continuous circulation is kept up in this way. Air was at first used in the rabble arms, but for oxidizing roasting, satisfactory for wet methods, it had to be abandoned.

The inner circular wall of the furnace has a continuous slot for the passage of the rabble arms. It is made reasonably tight by travelling steel shields, counterweighted so as to press gently against the walls forming the slot. The upper part of the wall, above the slot, rests on a casting suspended from I-beams and cross-beams, and braced by radial struts and angle irons. The I-beams are supported by the other wall and central column, and the cross-beams by the I-beams. The outer wall is 18 in. thick.

The rabble blades, which are made of 3/8-in. sheet steel, are graduated

in length and direction from the inner to the outer circle, so that the ore on the outer circle, which has to travel a greater distance, may be at the same height and remain in line with that near the inner circle. In other words, the rabbles are so proportioned that all the ore, through a cross-section of the furnace, travels uniformly through the furnace and is discharged at the same time, notwithstanding that the ore in the outer diameter has considerably further to travel.

In a furnace having an outside diameter of 60 ft., the smallest blade is 3/4×6×3/8 in., and the largest blade is 8×6×3/8 in., and the intermediate blades are proportioned to these dimensions. There are six rabble arms, and each rabble arm has 20 blades, for a hearth 10 ft. wide.

The rabble arms are fastened to the radial struts by a clamp which permits the raising or lowering of the rabble arm, so that the bed of ore may be kept level by raising or lowering the further end of the rabble. If the rabble is not properly adjusted, the ore may pile up on one side of the furnace, instead of having a uniform thickness.

The depth of the ore varies from 2 1/2 to 3 1/2 in., depending on the amount being roasted; 2 1/2 in. is the depth when roasting from 80 to 90 tons per day, and 3 1/2 in. when roasting 100 tons or more in a furnace having an external diameter of 60 ft. Such a furnace has six rabble arms, which make three complete revolutions in 5 minutes, or one revolution in 1 3/4 minutes. The ore is therefore rabbled every 17 seconds. The life of the rabble arm, which is a heavy 4-in. pipe, is one and one-half years. The life of the 3/8-in. sheet steel blades is three months in roasting low sulphur silicious ore, and from five to six weeks in roasting 30 to 40 per cent. sulphide ore. The blades are changed without cooling the furnace, and without interfering with the daily output of roasted ore. The rabble arms may be changed by cooling the furnace somewhat.

Two to three per cent. sulphur ore remains in the furnace from 2 1/2 to 3 hours, and on the cooling hearth, 1 hour.

The height from the top of the ore to the spring of the arch is 16 in., and from the spring to the crown of the arch, 12 in.

The Pearce furnaces, for sweet oxidizing roasting, are usually built with one roasting hearth above and a cooling hearth below.

The following gives a summary of data on the largest size Pearce roasters, Figs. 19 and 20, when roasting ores low in sulphur.

Outside diameter, 60 ft.
Width of hearth, 10 ft.
Average length of hearth, 168 ft.
Mean diameter of hearth, 53 1/2 ft.
Total hearth area, 1689 sq. ft. Available for roasting 1500 sq. ft.
Number of fireplaces, 4. Or 3 fireplaces and one oil burner.

Grate area of each fire place, 4 ft. by 4 ft. 8 in.
Number of rabble arms, 6.
Number of blades on each rabble arm, 20.
Angle of blades 22 1/2 degrees.
Depth of ore, from 2 to 3 1/2 in.
Rabbles make one revolution in 100 seconds.
Ore stirred every 17 seconds.
Capacity per 24 hours, roasting 2.5 to 3.0 per cent. sulphur ore down to 0.5 or 0.75 per cent., 100 tons.
Power required to drive furnace, 6 h. p.
Fuel required, 10 tons good bituminous coal.

The Holthoff-Wethey Furnace.—The Holthoff-Wethey furnace, shown in Figs. 21 and 22, is regularly constructed with a roasting hearth above and a cooling hearth below. The roasting chamber is supported on structural steel, arranged so that there is a space between the side walls of the furnace and the supporting posts. In this space, on both sides, and attached to the posts are the tracks for the rabble trucks, running longitudinally with the furnace. The rabble trucks are mounted on chains, which are moved, raised, and lowered by sprockets at both ends of the furnace.

The power for driving the mechanism is applied to the shaft at one end of the roaster on which one pair of sprockets are mounted. The driving mechanism, rabble trucks, chains, and tracks are all located entirely outside of the roasting chamber and at all times exposed to the air. The slot through which the rabble arms pass are opened and closed automatically by tripping doors, or flexible steel sheathing, as the rabble progresses through the furnace. One half of the number of rabble blades of each rabble are set at one angle and half at an opposite angle, thus removing all end thrust.

The reverberatory arch is firmly held in place between two heavy I-beams, suspended from above and from beams resting on the channel iron posts. Opposite posts are securely joined together and take the end thrust of the arch.

The ore is fed evenly into the furnace at the drive end, and after travelling the full length of the roasting chamber, is dropped to the cooling hearth and again carried back to the charging end, thus allowing the ore the same time to cool that was required to roast it. The cooling hearth may be provided with water pipes or water jackets to help cool the ore, but this, on account of the length of the cooling hearth, will usually not be necessary.

The furnaces are usually built from 10 to 12 ft. wide and from 100 to 130 ft. long. The ordinary dimensions are 12 × 120 ft. Such a furnace, for roasting ores low in sulphur, is equipped with eight rabbles, which

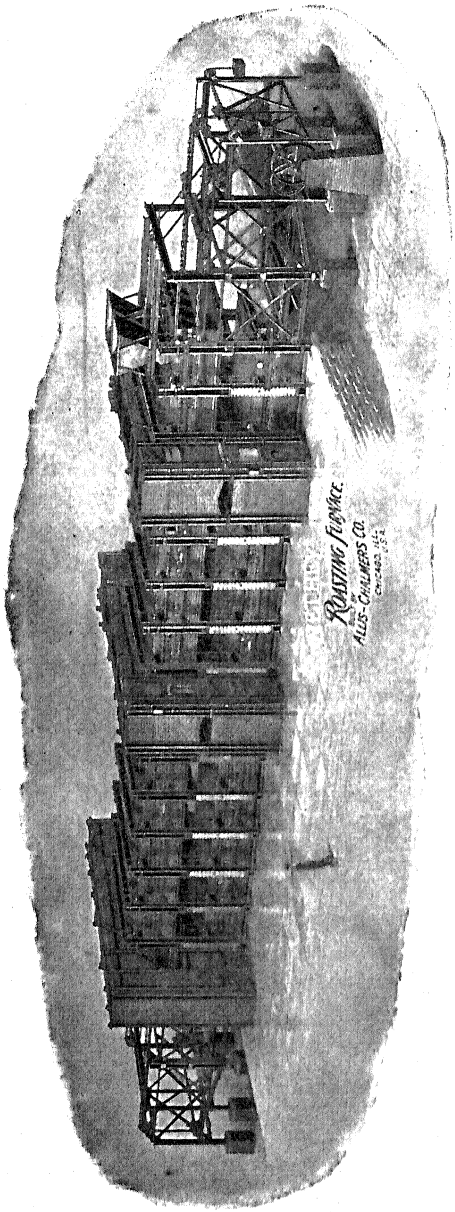


FIG. 21.—Holthoff-Wethey furnace. Perspective view.

make a complete revolution in 4 1/2 minutes, thus stirring the ore every 33.5 seconds. The upper sprocket shaft, at the drive end, is counterweighted so as to keep the rabble chains taut.

The iron work for a 10 × 100 ft. Holthoff-Wethey furnace, with roasting and cooling hearths, weighs approximately 130,000 lb. Such a furnace usually has four fire-boxes and a grate area of 60 sq. ft.

In the erection of this size furnace there were required:

68,000 common brick,
4,000 fire brick.

It was driven by a 15 h. p. motor.

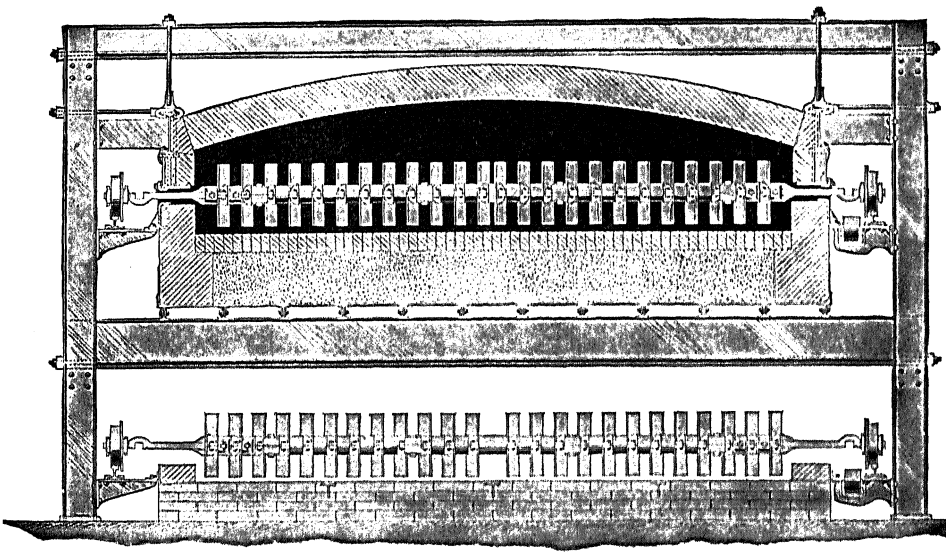
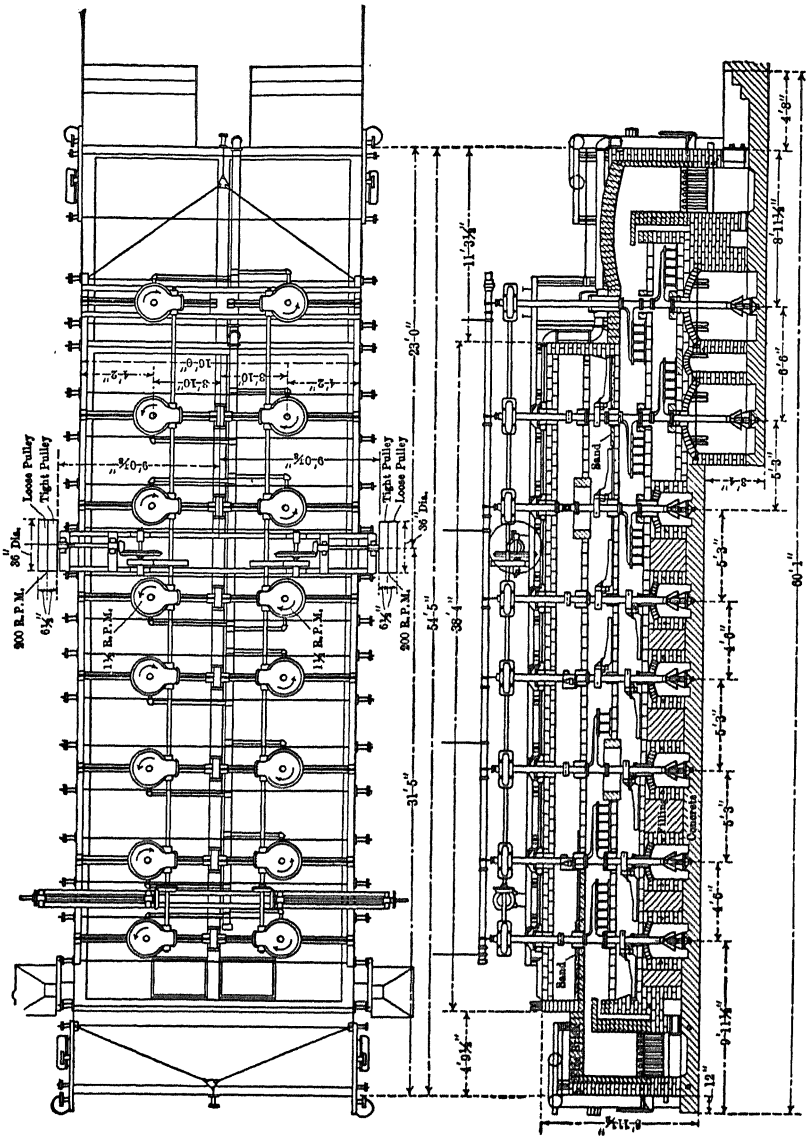


FIG. 22.—Holthoff-Wethey furnace. Transverse section.

This size furnace erected at Dalonega, Georgia, roasted concentrates containing over 15 per cent. sulphur down to 0.15 or 0.20, all but a trace of which was as soluble sulphates. The capacity was 35 to 40 tons per day of 24 hours. The ore contained 10 to 12 per cent. moisture when charged into the furnace. The fuel used was 12 cords of wood, which for 35 tons per day would equal 0.34 cord per ton. At Colorado City six Holthoff-Wethey furnaces, 12 ft. wide and 120 ft. long have been in operation for many years roasting Cripple Creek ores for chlorination, with a capacity of 100 per furnace per day.

The Merton Furnace.—The Merton furnace, Figs. 23 and 24, is a rectanguiar multiple hearth furnace in which the rabbling is done by vertical shafts arranged in a line, and passing through the respective hearths. To these shafts are attached rabble arms of a radius equal to



FIGS. 23 and 24. Merton furnace. Plan and longitudinal section.

one-half the width of the furnace. The vertical shafts are a little further apart than the radius of the rabble arms, so that their areas of revolution intersect, and the ore is delivered from one rabble to the next, through the different hearths.

Each shaft is set in motion by a worm gear or by spur and pinion, and arranged to revolve at the desired speed—usually from one and one-half to three times per minute. A rabble arm is attached to each shaft for each hearth. In the adjacent hearths the rabbles on each shaft are placed at right angles to one another. Three of the rabble arms in the same hearth are made to point in the same direction, while the fourth, or end rabble, is at right angles to them.

The finishing hearth has a special rabble to itself which is larger than those working on the other hearths; it may be water cooled, but for ores not requiring a high finishing temperature the water cooling is often dispensed with.

The entire furnace is enclosed in 1/4-in. plates, well braced with buckstaves and rods.

For a standard type furnace the total length is 32 ft. 6 in. The main body of the furnace measures 23 ft. 9 in. long inside the plates, 8 ft. wide, and the height, with three hearths, is 6 ft.

The hearths are horizontal, and are not given any inclination whatever. The height from the hearth to the crown of the arch, inside measurements, is 16 1/2 in., and 9 in. at the sides. The thickness of the crown of the arch is 4 1/2 in. Each of the hearths has a door opposite each shaft. At the end of each hearth is a slot connecting with the hearth below.

In roasting, the ore is fed in at one end of the upper hearth, and passed from one rabble to the next until it reaches the other end, where, discharging through the slot, the ore is delivered into the next hearth below, and is carried by another series of rabbles to the opposite end, again it is discharged to the third hearth and travels along it to the finishing hearth. Near the end of the third hearth is another slot in which is a gate permitting the control of the discharge to what is termed the finishing hearth. In this hearth the roast is completed.

The weight of the iron work of this furnace is about 12 tons. About 10,000 ordinary brick and 3000 fire bricks are required in its construction. About 2 h.p. is required to drive the mechanism.

The Edwards Furnace.—In the Edwards furnace, Figs. 25, 26 and 27, the ore is advanced by a series of revolving rabbles of relatively small diameter and of intersecting areas, so that the ore from the first rabble is delivered to the next, and so on through the series until it issues as the roasted product.

The furnace is regularly made in two general types; one having a single row of rabbles, known as the "Simplex," and the other having a

double row of rabbles, known as the "Duplex." These two types are built either "Tilting" or with "Fixed Hearth." In the tilting construction there is a double continuous girder, balanced on a center support. The girder supports the iron work of the rabbling mechanism and the drive therefor. The furnace is adjusted vertically at the end

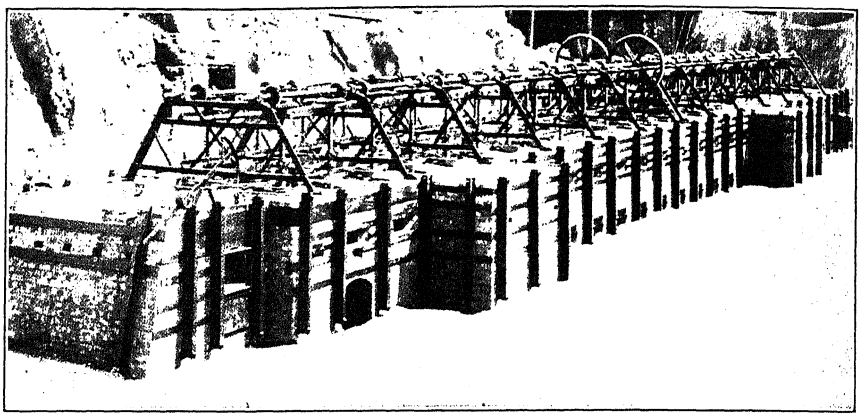


FIG. 25.—Edwards furnace. Perspective view.

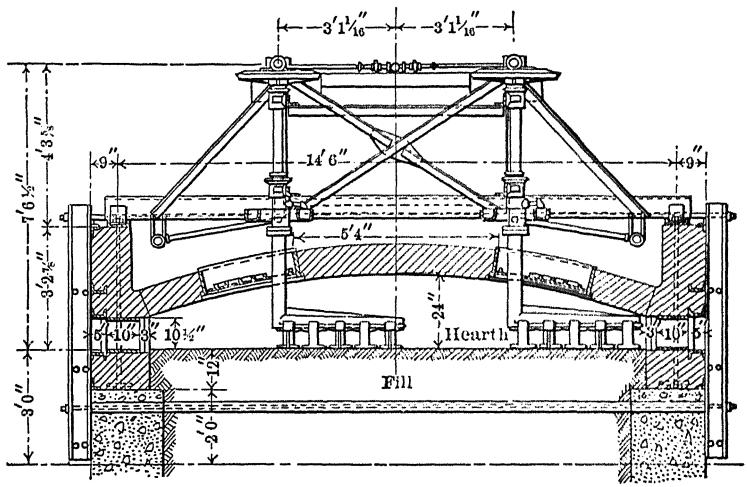


FIG. 26.—Edwards furnace. Transverse section.

to give the hearth any desired slope. The iron construction is encased in brick. The fixed hearth construction is the same as in standard reverberatory practice.

The *tilting* furnace is a straight single-hearth reverberatory, 63 ft. long by 9 ft. wide over all, and 58 ft. by 6 ft. 5 in. in the clear, which is

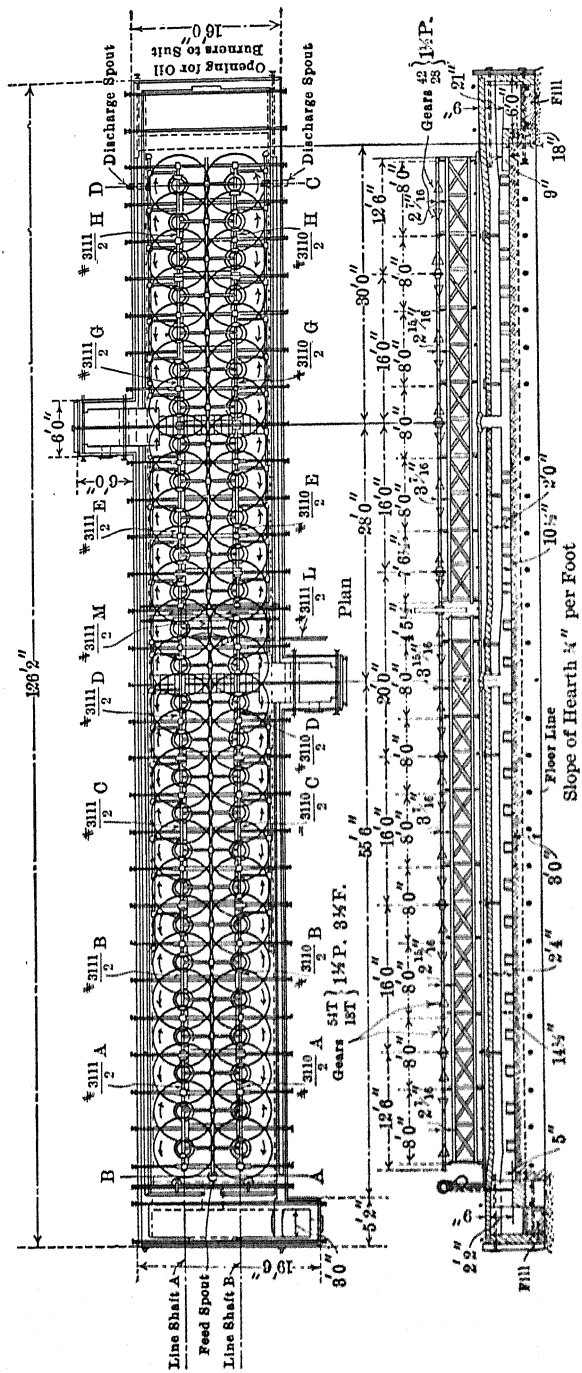


FIG. 27.—Edwards furnace. Plan and longitudinal section.

designed for sweet roasting of concentrates or sulphide ores. The shell of the furnace is a rectangular chamber of plate-iron stiffened with angle iron; this is lined inside with brick. Good common red brick are found suitable for ordinary temperatures, although at the fire end fire bricks may be used. 10,000 bricks are required for the lining of this furnace.

On top of the furnace is mounted gearing for driving the rabbles, the spindles of which extend down through the cast-iron boxes, built into the brickwork of the reverberatory arch. The whole furnace rests on two pivots, one for each side. These pivots are arranged near the middle of the length of the furnace, so that by tilting the furnace from the horizontal to various angles, the discharge of the ore may be regulated according to the rate at which it is being roasted. The mechanism for tilting the furnace is simple, and can be worked without altering the usual speed of the rabbles. The weight of the whole iron work including the shell, bracing, shafting, gearing, rabbles, etc., is 19 tons. No single part of the furnace exceeds 2500 lb. in weight, while most of the parts do not exceed 225 lb.

The bottom of the furnace is supported on No. 14 corrugated steel; directly on this is placed a thin layer of non-conducting material, and on this is laid the brick floor.

There are 15 rabbles placed side by side along the length of the furnace, the blades of which nearly touch the hearth. Each rabble has a circular path, the circumference of which almost touches the brickwork on either side, and as the distance between the rabbles is a little greater than the radius of the circle described, each rabble works ore almost up to the heel of its neighbor, and as each rabble rotates in the opposite direction to the one next to it—they are alternately right- and left-hand rabbles—the ore is not passed along too rapidly from one end of the furnace to the other, but gets a thorough stirring and exposure to the air as it proceeds on its course.

The speed of the first 13 rabbles from the feed end is one revolution per minute, while the fourteenth has two, and the fifteenth, or discharge rabble, four revolutions per minute. All the rabbles being driven from the same shafting, the change in speed is arranged by alternating the ratio of the bevel wheels. The speed of the fourteenth and fifteenth rabbles is so arranged that while they stir into the areas of the adjacent rabbles, they do not come in contact with them. The object of this increased speed is to give the ore a brisker stirring in the final stages of the roast.

In order to protect the rabbles in the hottest part of the furnace from the destructive action of the high temperature, water is circulated through the last three to keep them cool; by this means they are found to last for years.

There are two different kinds of rabbles used; one is solid and flat-

footed, the front edge of which is beveled; the other is hollow; on the arm of it cast-iron shoes are fitted. The latter rabble is the one used at the fire end of the furnace. The cast-iron shoes can be slid on or off the rabble arm without lowering the heat of the furnace or removing the rabble from it. When roasting concentrates or ores high in sulphur, the first 10 rabbles, counting from the feed end, are generally of the solid, flat-footed type; these pass through the ore close to the hearth and effectively stir and expose the particles of ore so long as they carry a fair percentage of sulphur. The last five rabbles are provided with cast-iron shoes, as by the time the ore reaches this part of the furnace it has lost most of its sulphur and is less lively. These shoes pass through and under the ore.

When roasting ores that do not contain much sulphur, shoes are used on all the rabbles, although water need only be circulated through those subjected to the greatest heat. The ordinary flat-footed rabble arm is fastened to the spindle by placing the end in a socket and passing a pin through both. The water rabbles have a 3 1/8 in. cast-iron hollow spindle with a flange at the bottom, which is bolted on to a corresponding flange on the upper part of the arm.

The ore is conveyed by an automatic feeder from the hopper into the hearth at the upper end of the furnace; after traveling to the lower end, near the fire, the ore is discharged down a pipe, located near one of the sides; the bottom of this pipe passes through and works in a case leading to the conveyor, to prevent any escape of dust. This conveyor pushes the ore into the pit.

During the roasting air is admitted through the holes, situated above the fire bars. The fumes pass into the main flue through a short flue, which is attached to the furnace. To allow for the movement of this short flue when the angle of the furnace is altered, the hole in the main flue through which it passes is made larger than actually required for a nice fit; in order to cover the space left between the short and main flues, and prevent cold air from passing into the latter, a sliding cover-plate moves in a frame, which is bolted onto the brickwork of the main flue.

The power required to work the furnace is from 2 to 3 h. p.

The *Duplex* furnace is a stationary structure, designed for large capacity. The principle of rabbling is similar to that adopted in the tilting furnace, but consists of two lines of rabbles driven from two horizontal line shafts, and the walls can be built of brick or concrete. The concrete can be brought to within two layers of brick to the fire zone. The brackets carrying all the mechanical superstructure are firmly fastened to anchor bolts in the furnace walls, and angle stays and cross bars are so arranged as to make the entire superstructure firm and substantial. Buckstays and tie rods hold the whole of the arch and

brickwork together with straps on the face of the walls to give solidity to the skewbacks to protect the arch.

This furnace when complete and ready for operating consists of 100,000 lb. of iron and steel and 70,000 bricks. Fire bricks are only used when in close proximity to the fire-box.

The hearth area of the standard Duplex type, 112 ft. long by 13 ft. wide gives 1456 sq. ft. of working area, and the outside measurement overall is 116 ft. by 16 ft.

The usual fall of the hearth in this furnace is 1/2 in. to 1 ft., and the mechanism driving the furnace can be so arranged to drive the rotating rabbles at various speeds so that the roasting material can be under the control of the roasterman.

The furnace requires from 6 to 9 h. p. to operate, according to the speed at which the rabbles are driven.

The water required to cool the rabbles is 400 gallons per minute.

The McDougal Furnace.—The McDougal Furnace,[1] has long been used to roast copper ore and concentrates for smelting, and has been modified by Herreshoff, Evans, Klepetko, Wedge, and others to adapt it to modern requirements. This furnace, so successful in imperfectly roasting copper ores for smelting, has recently been improved to adapt it to the more thorough roasting required for the hydrometallurgical processes.

The McDougal furnace, Figs. 28 and 29, is essentially a multiple hearth upright cylinder with central shaft carrying the radial rabble arms. The hearths are horizontal arches having discharge openings alternately at the center of one hearth and the periphery of the next. The central revolving shaft is provided with radial rabble arms for the different hearths, and the rabble blades are so arranged at an angle with each arm that for the odd numbered hearths they push the ore toward the center, and on the even numbered hearths toward the periphery. In doing so the ore is turned over and over by the rabbles and describes a spiral course around the shaft. The ore, in its descent from hearth to hearth, describes a zig-zag course through the furnace from top to bottom, passing alternately through the holes at the center and at the periphery.

The size of the McDougal furnaces, as largely used at Butte, is 16 ft. in diameter, and 18 ft. 3 1/2 in. high. It is sheathed with 3/8-in. boiler iron and lined with a full course of red brick. It has six arched hearths with a 9-in. spring and 3 ft. apart; each hearth has two rabble arms making one revolution per minute. Each furnace has two exhaust flues 24 in. in diameter and 12 ft. apart, passing out of the roof, and flues from three furnaces lead to one main 6 ft. in diameter, having openings along the top and bottom for removing the flue dust.

[1] H. O. Hofman, Trans. Am. Inst. Mng. Eng., Vol. XXXIV; L. S. Austin, Tras., Vol. XXXVII; Peters, "Practice of Copper Smelting."

The central shaft of the furnace is driven from below. The cooling water for the rabbles is forced down to near the bottom of the revolving hollow shaft, which is 9 in. in diameter, through a 3-in. pipe and out to the ends of the horizontal rabble arms through 1-in. horizontal pipes. In its upward passage between shaft and pipe it takes up the return

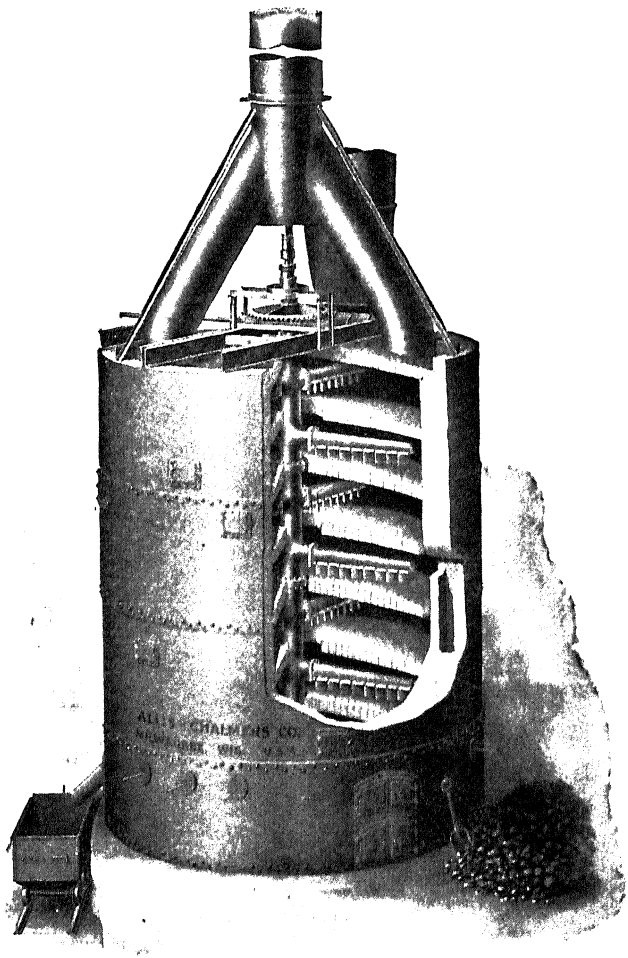


FIG. 28.—Allis-Chalmers McDougal furnace (fire-box type). Perspective view and section.

water from the rabble arms and discharges at the top through two spouts into a secondary launder. Shafts and arms are made up of flanged sections to permit of easy exchange. Running the overflow water at 80° F. 20 gallons of cooling water are required per minute to cool the rabbles.

The two rabble arms of a hearth have seven and eight cast-iron blades; these are 8 in. long and 6 in. wide, and 5/8 in. thick; the lower 12 in. of the blade which comes in contact with the ore are chilled. The blades on the top hearth last from 25 to 35 days; those on the sixth, from 6 to 8 months.

The six circular flat arches which form the roof of one hearth and the floor of the next above, require care in construction. There must be a large central opening for the main vertical shaft which carries the rabbles, and the brick at the periphery must be well anchored. There must also be drop holes from each hearth to the next, and these are

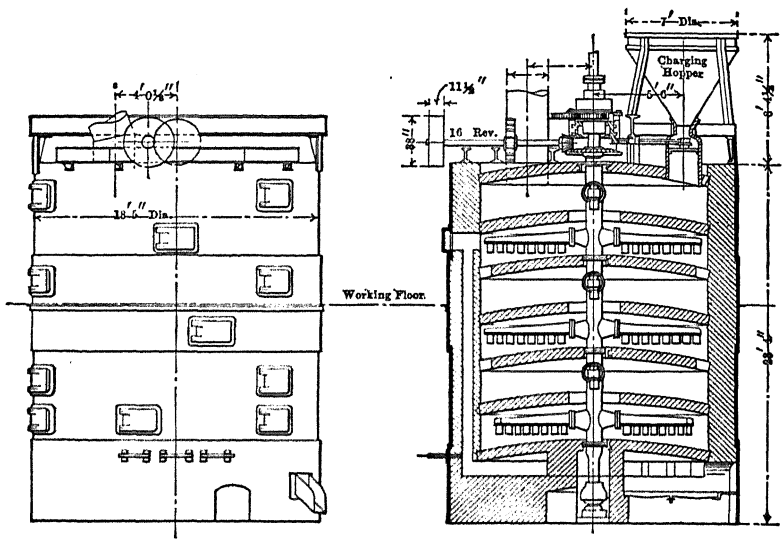


FIG. 29.—Elevation and section. McDougall roaster.

arranged alternately at the central opening and at the extreme periphery of the hearths and protected by iron castings. The first, third and fifth hearths have one drop hole at the center; the second and fourth have six and the sixth has two drop holes near the periphery.

The hearths with peripheral openings are provided with a central cast-iron ring, cut in halves. This ring circles the shaft, leaving an annular clearance space of 3 in. The brick of the hearth butts against the exterior of this ring in its entire circumference, and is keyed into a groove in the ring. The center drop hole is formed by stopping the brickwork of the hearth so as to leave an annular space of 16 in. encircling the shaft. The peripheral drop holes are 14 in. wide on the first and fifth hearths and 18 in. wide on the third hearth, where there is a strong evolution of sulphur gas.

In roasting at the Washoe smelter at Butte, the moist concentrates

are dumped into the feed hopper on top of the furnace, which holds 33 tons. The composition of the material is:

Moisture,	8.1 per cent.
Cu,	7.42 per cent.
SiO_2,	21.2 per cent.
Fe,	26.1 per cent.
S,	33.2 per cent.
Al_2O_3,	2.7 per cent.
CaO,	0.3 per cent.
	98.94 per cent.

To this is added 5 per cent. of limestone, of which the diameter of the largest piece does not exceed 1 in.

The ore is fed continously into the furnace and is spread on top of the hearth to the thickness of 3 in. by the rabbles. The ore dropping down through the holes in the hearths showers through the ascending air, which actively roasts it, but at the same time this air current carries away the finer particles as dust, which amounts from 4 to 5 per cent. of the ore charged. The gases escaping from the upper hearth have a temperature of 315° C.; by the time they reach the flue chamber they have cooled to 117° C.

The appearance of the roasting at the different hearths is as follows: On the first hearth the ore is dropped at the circumference and, containing 6 to 10 per cent. moisture, is drying out, but attains no visible heat. Entering the second hearth it still looks dark, but shows a blue flame by the time it reaches the borders of the hearth, where it is 600° C. On the third hearth some sparks show where the rabble passes, together with blue flame, and with a flame temperature of 900° C. On the fourth hearth the sparking has ceased, the ore having attained an orange-red heat. In falling upon this hearth from the one above, the ore as it showers down burns freely, hastening the roasting by this momentary, but thorough exposure to the ascending tir. On the fifth hearth the sulphur is eliminated sufficiently so that the discharge temperature is less than the entering temperature; that is, the ore is brighter near the periphery than at the center. On this hearth, the maximum temperature of 960° C. is attained. On the sixth and final hearth the heat has become uniform, but is lowered to 860° C. As the ore leaves the hearth it seems brighter, but speedily cools to 660° C. as it falls, smoking freely, into the hopper. Fig. 30 shows diagramatically the progress of reactions and temperatures.

The composition of the escaping gases is:

	By weight per cent.	By volume per cent.
SO_2,	4.95	2.25
SO_3,	1.46	0.53
O,	19.60	18.45
N,	75.00	78.77

Thirty-two pounds of air is needed per pound of sulphur and since 13.3 lb. of the latter is burned off per minute, there is needed in that time 6384 cu. ft., which passes up the central hearth openings at the rate of 8.8 ft. per second. A screen analysis of the flue dust shows:

On 10 mesh screen,	9.7 per cent.
Between 10 and 30,	25.3 per cent.
Between 30 and 80,	30.7 per cent.
Passing 80,	33.4 per cent.
	99.1 per cent.

The ore takes about 2 hours and 15 minutes to pass through the furnace.

In starting up a furnace, a small fire of dry, soft, long flame wood is started from the three side doors of the third and fifth hearths. A new

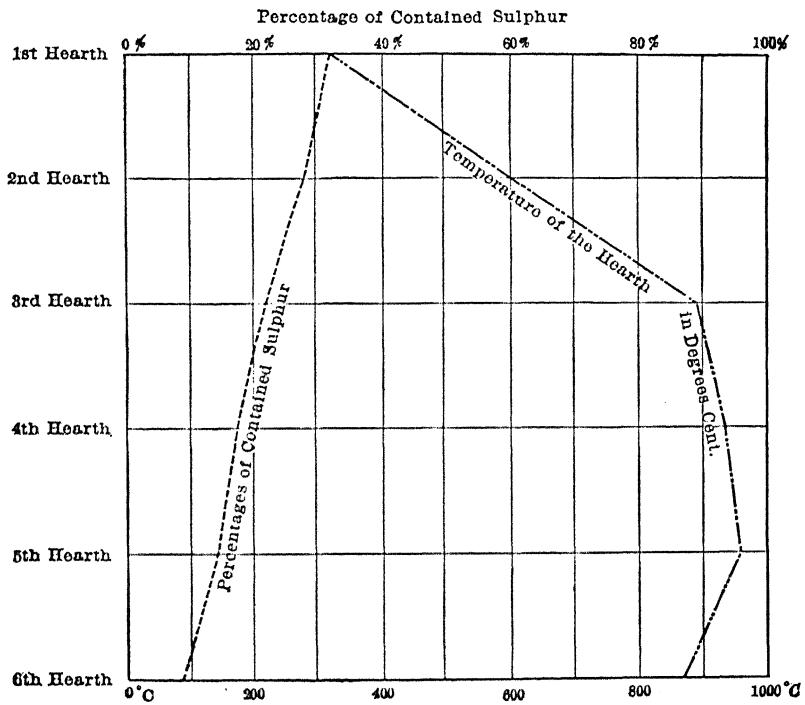


FIG. 30.—Progress of reactions and flame-temperature in the McDougall roaster.

furnace is brought to a dark red heat in 3 to 4 days, an old furnace requires only 2 days. Concentrates are then fed. After charging for 5 or 6 hours, it sometimes happens that the furnace cools down too much, and this makes it necessary to start on the third and fifth floors a new fire for 1.5 to 2 hours; occasionally feeding of the ore is stopped and half a ton coal charged. Under normal conditions a furnace does its best work when the flue shows a depression in water of 0.3 in. If it is

less the furnace gets cool. The temperature may be regulated by the admission of air; closing the bottom doors drives up the heat, opening the doors draws it down; opening doors higher up checks the draught. The rate of feed once settled upon is usually not altered, and the number of revolutions the rabbles make per hour remains the same.

A section of six furnaces is tended to in 8-hour shifts by one-third foreman, one furnaceman, one helper, one-sixth oiler, and one-ninth repair man and one trimmer.

The dust which collects in the flues connecting the furnaces forms 4 to 5 per cent. on the ore, is raked out every day. The loss in weight, including the flue dust, is about 20 per cent.

A furnace treats under normal conditions, 40 tons of sulphide ore, with 35 per cent. sulphur, and 10 per cent. copper, or 0.042 tons per square foot of hearth area, reducing the sulphur to 7 per cent. Roasted ore with 14 per cent. copper treated in the same manner, retains about 10 per cent. sulphur. The product can of course be varied with the speed of travel of the rabbles, and the sulphur more thoroughly eliminated by the addition of fireplaces.

The following partial analysis of roasted ore represents two determinations from the average day and night samples taken during an experimental run of 15 days. SiO_2, 26.9 per cent.; Cu, 18. 3 per cent. of which 9.9 per cent. was present as CuO; Fe, 30.0 per cent. of which 17.9 was present as FeO; S, 9.3 per cent. of which 0.81 was present as SO_3.

At Butte, in the regular roasting of concentrates the results are:

Amount roasted in 24 hours,	40 tons.
Sulphur in raw concentrates,	35 per cent.
Sulphur in calcines,	7 per cent.
Hearth area,	952 sq. ft.
Concentrates roasted per square foot of hearth area,	84 pounds.
Coal,	none
Cost of roasting,	35 cents.

The large sizes of the st
diameter of 18 ft. 5 in., cont
under the sixth hearth. Th
a furnace is about 90,000 l
about 37,000 red brick and

At the Washoe smelter
McDougal furnaces are in o
and an outside diameter of 1
3/8 in. thick and are lined
inside hearth diameter of 14

At Garfield, Utah, where
ore and concentrate mixture
sary to roast below 10 or 1

[1] R. R. Moore, *E. and M. J.*, M

per cent. of the total charge was added on the fifth hearth, which gave an average of 55 tons per day at a cost of 22 cents per ton. Other averages of over 50 tons per furnace day were maintained for six months at a cost of less than 25 cents per ton. The concentrates added on the fifth hearth of the McDougals were high in copper. They were added there on account of the fineness and tendency to produce excessive amounts of flue dust. At Garfield the McDougals produce about 6 per cent. flue dust. This flue dust carries more silica and sulphur and less copper than the charge. Notwithstanding the elaborate system of flues constructed at the Garfield plant there was a stack loss of about 500 lb. of copper per day from these roasters.

The McDougal furnaces are regularly built in the "Self-roasting" and "Enclosed Fire-box" type. If a more thorough roast is desired in the self-roasting type for hydrometallurgical work than can be obtained without fuel, satisfactory results are obtained by firing with oil, in which case the oil is injected into the various hearths, as desired. If solid fuel is used, it is desirable to use the enclosed fire-box type. This type has two grates at the bottom, each having an area of 29 sq. ft. or a total area of 58 sq. ft. of grate surface to each furnace. In one furnace of the enclosed fire-box type, partly muffled, for roasting pyritic ore containing 45 per cent. sulphur and reducing it to an average of 2 per cent. in the calcines, there is obtained a capacity of 14.4 tons per day of 24 hours.

The Herreshoff Furnace.—In this furnace, Fig. 31, when used in roasting pyrites for sulphuric acid manufacture, or for the preliminary roasting of sulphide ores for metallurgical treatment, the rabbles are cooled with air, through the central column. This column in a double vertical hollow shaft. Attached to this shaft are one or more arms at each hearth, and the replacable rabbles are slipped on these arms. The air for cooling the rabbles is forced into the bottom of the column and then delivered through the central part of the shaft, from which it passes in multiple at once to all the arms. After cooling the arms it returns to the annular space between the inner and outer shaft, and finally discharges at the top of the outer shaft.

The temperature of the iron in the shaft and arms is kept above the condensing point of acid to prevent corrosion, and at a point where the strength of the metal is the greatest. The rabbles are made in sections. There are five sections on each arm of from one to five blades per section, depending on their position on the arm. The sections can be slipped on or off the arms and any blade can be taken out of the section and replaced without disturbing the rest. The hearths are made of special moulded arch fire brick.

The shaft is driven from the bottom by means of a cast iron gear and pinion, and makes one revolution in from 70 to 150 seconds, depending on the kind of roast. The six-hearth furnace, 15 ft. 9 3/4 in. diameter,

requires about 1 h. p. Speed reductions are made by gear, reducing worm gear, or sprocket, as desired. A shear pin is provided in the driving mechanism which acts as a safty device in case of undue strain. The following table gives dimensions and data for some of the standard size furnaces.

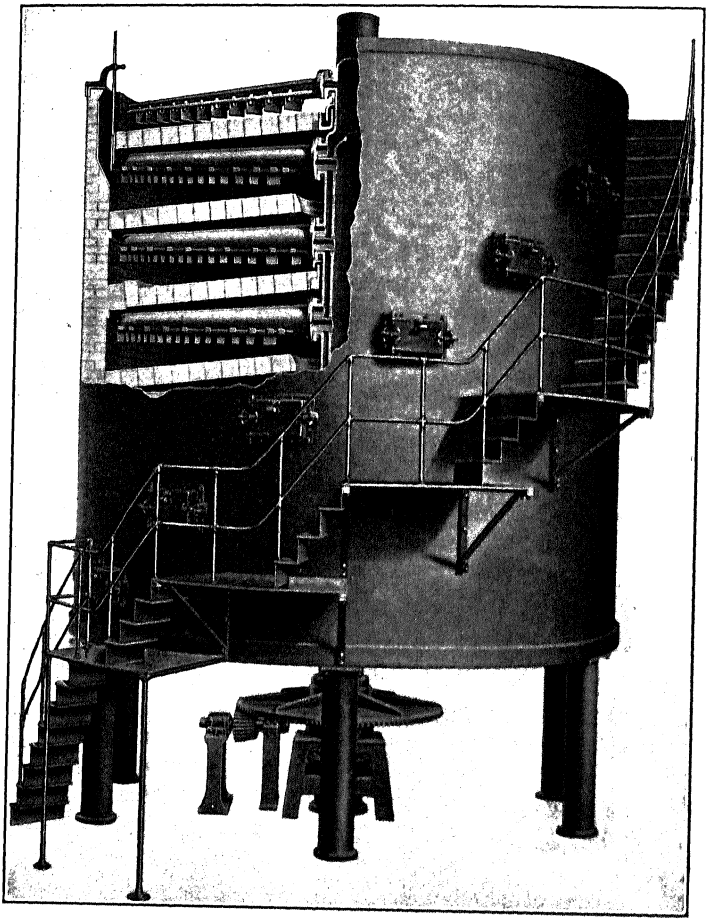


FIG. 31.—Herreshoff furnace.

HERRESHOFF FURNACE

Outside diameter	Number of hearths	Hearth area square feet	Weight, metal parts	Weight, special fire brick	Pounds, sulphur per 24 hours
11 ft. 7 1/2 in.....	5	381	16,000 lb.	16,000 lb.	3,000 to 6,000
11 ft. 7 1/2 in....	7	547	25,000 lb.	32,000 lb.	4,500 to 12,000
115 ft. 9 3/4 in...	6	912	43,000 lb.	79,000 lb.	8,000 to 21,000
20 ft.....	5	1,308	68,000 lb.	132,000 lb.	12,000 to 30,000
20 ft.....	7	1,810	82,000 lb.		

In the above tables the capacities given in pounds of sulphur per 24 hours must be used to form a general idea only, as the chemical composition and physical character of each ore, together with the kind of roast required, will have to be determined for each particular case.

The Wedge Furnace.—The Wedge furnace, Figs. 32 and 33, has for many years been successfully used in the east for chloridizing roasting

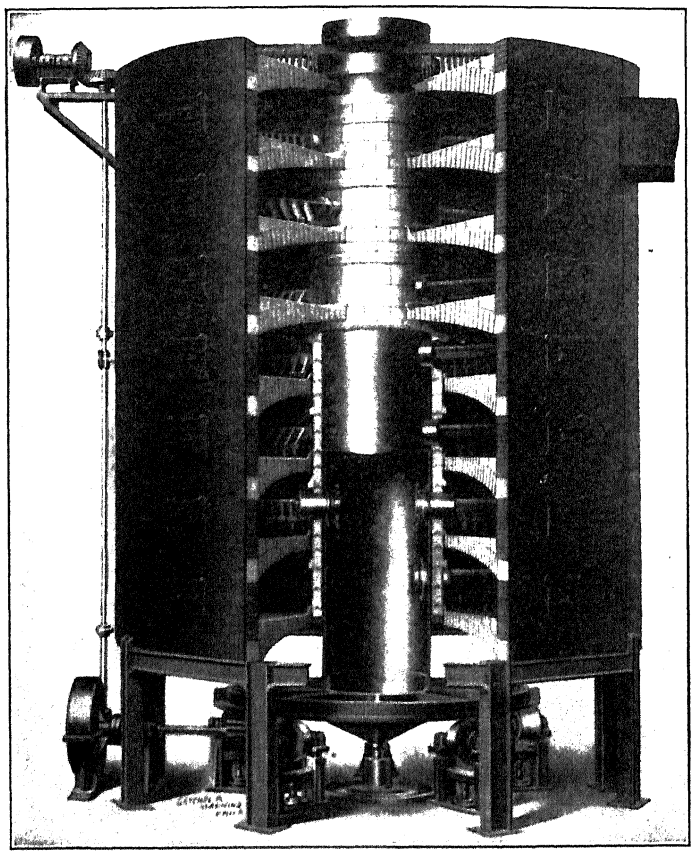


FIG. 32.—Wedge furnace.

copper ores, and its use is rapidly being extended into the field of oxidizing roasting. The Wedge furnace is of the McDougal type and built in various diameters, with one, three, five, or seven hearths, as may be required. The top of the furnace is used as a dryer, and a bottom hearth, below the roasting hearths, may be used as a cooler.

The ore or concentrate is fed to the top of the furnace at the periphery, and is mechanically fed across the top, entering the center of the

furnace dry and hot. The feed entering the furnace is so arranged that the material forms a lute, making the furnace gas-tight at this point.

One of the most distinctive features of the furnace is the central shaft which is hollow, open at the top and bottom, 4 ft. in diameter, and is covered with tile which are attached to and revolve with the shaft. The advantage of the large hollow shaft is that an arm can be changed easily and without losing heat in the furnace. The arms are held in position by breech blocks placed upon the inside of the central shaft; this makes it possible for workmen to enter the central shaft while the heat is in the furnace, and remove the breech block, when workmen

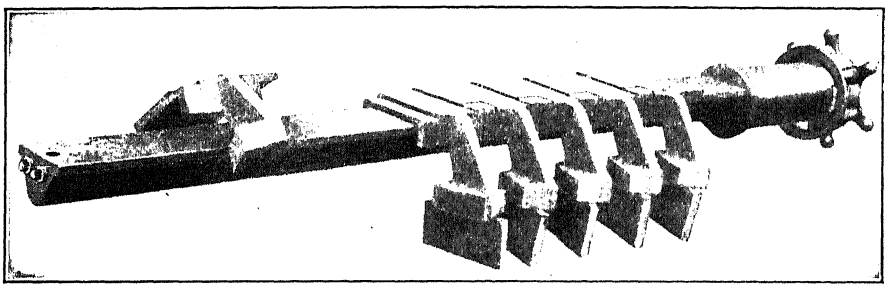


FIG. 33.—Rabble details, Wedge furnace.

on the exterior of the furnace will withdraw the wornout arm through one of the doors and insert a new arm, when the workman on the inside of the shaft will replace the breech block. All parts in connection with the rabbling mechanism are interchangeable.

The arms are built for either water cooling or air cooling. Each arm has its own supply pipe and discharge pipe, so that it is possible for the furnace operator to know at all times that each arm is receiving its proper supply of water.

The hearths are all level. This is made possible by building them of specially shaped fire brick. These are pressed brick and the arches are laid up dry. The result is that falling arches are eliminated. In furnaces which have been in operation for eight years, the arches are still in good condition without the expenditure of one dollar for repairs.

The weight of the central shaft and arms, including the arms on the dryer hearth, is carried on roller bearings. This reduces the power required to operate the furnace to a minimum. The indicated power on a large 21 ft. 6 in. diameter furnace, with seven hearths, is less than 2 h. p.

The furnace is built with either a full steel shell or skeleton construction, as may be desired. Common red brick may be used in the side walls. The furnaces may be fired with oil, gas, or solid fuel. When solid fuel

is used the fire-boxes are placed at the sides of the furnace, and the heat or gases to the various hearths regulated by suitable dampers.

The single hearth chloridizing furnace, made for direct firing with oil, is 32 ft. in diameter and has a capacity of 100 tons of pyritic cinder per day of 24 hours. The fuel used is 14 gallons of oil or 210 lb. of coal, per ton of ore roasted, or approximate 10 per cent. of coal on the weight of ore.

The multiple hearth muffle fired furnace has been successfully used for sulphating roast, in which, on some ores, 88 per cent. of the copper was soluble in water. By the use of a weak acid, which can be made at low cost from the escaping gases, the extraction has been increased to 98 per cent.

The rabbles and rabble arm, Fig. 33, can easily and quickly be removed and replaced.

The furnaces are built both with open hearth or muffle, and of varying diameters and number of hearths. The following table gives the essential figures for some of the standard sizes.

No.	Diameter outside	Number of hearths, sq. ft.	Hearth area, sq. ft.	Weight of metal parts, lb.	Capacity in 24 hours, tons of 2000 lb.	
1	9 ft. 9 in.....	5	217	18,075	2.5	10.8
2	9 ft. 9 in.....	7	304	22,075	3.5	15.0
3	12 ft.....	5	373	22,200	4.3	18.6
4	12 ft.....	7	522	26,600	6.0	26.1
5	16 ft.....	5	725	76,500	8.3	36.0
6	16 ft.....	7	1015	91,800	11.6	51.0
7	20 ft.....	5	1245	97,000	14.3	62.0
8	20 ft.....	7	1743	113,000	20.0	87.0
9	21 ft. 6 in.....	5	1470	101,200	16.9	73.5
10	21 ft. 6 in.....	7	2058	118,000	23.6	103.0
11	22 ft. 6 in.....	3	978	76,300	11.2	48.9
12	32 ft.....	1	787	154,400	100	

No. 12 furnace is designed more especially for chloridizing purposes, and the capacity shown above has been demonstrated in this service.

In the capacity column the figures at the left are based on roasting pyrites containing 50 per cent. sulphur, and reducing the sulphur to 2 per cent. in the roasted ore.

The figures at the right in the capacity column are based on smelter practice where concentrate containing 35 to 38 per cent. sulphur is roasted, the sulphur being reduced to from 7 to 9 per cent.

When oil is used as fuel it can be introduced through port holes anywhere at the sides of the furnace, as in Fig. 32; if coal is used, regular fire-boxes are necessary, as shown in Fig. 41.

The Greenawalt Porous Hearth.—The porous hearth, Fig. 34, inventey by John E. Greenawalt, and patented in 1906, is applicable to and

furnace. Some rather remarkable results have been obtained in roasting ores by the use of this device, both as to saving of fuel and capacity per square foot of hearth area.

The essential principle involved is the method of supplying sufficient air for the ready oxidation of the incandescent sulphide particles not directly exposed to the oxidizing atmosphere of the roasting chamber. One of the greatest objections to reverberatory furnaces is that the heat and air cannot be most effectively applied. The top layer of the ore is

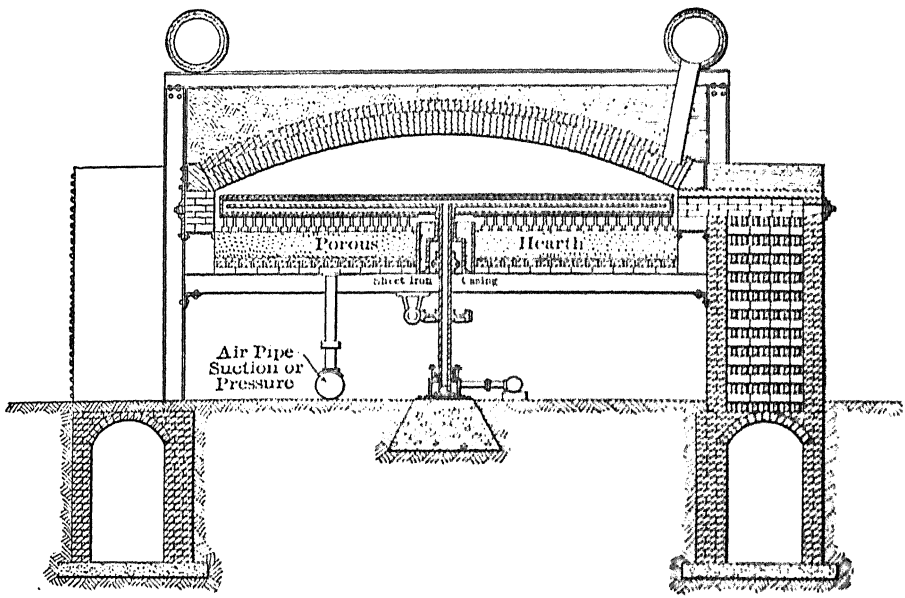


FIG. 31.—Greenawalt porous hearth furnace.

exposed to the highly oxidizing atmosphere, but that below the surface is in an atmosphere which, if not reducing, is certainly not highly oxidizing.

To obviate these difficulties Greenawalt conceived the idea of placing the roasting ore on a porous bed, or filter, and percolate the air, either up or down, through the ore mass and porous bed. In carrying out the first experiments in a hand reverberatory furnace, certain interesting results were obtained. The air, in roasting heavy sulphide ores, was not found to be of much benefit in the early stages of the roasting, but in the later stages it proved of the greatest advantage. Another difficulty in roasting heavy sulphide ores was that the oxidizing effects were so violent that the heat evolved sintered the charge so that the sintered portion had to be screened from the roasted ore before it was learned how to properly regulate the draft or suction. The sintering, or agglomeration, was entirely due to the air supply, so that if the ore was to be

roasted without agglomeration, the air was percolated through the ore and porous bed with moderation, while if agglomeration or sintering was desired the air was used with considerable suction or pressure, depending upon whether down-draft or up-draft was employed. Roasting, with or without sintering, was found to be purely a matter of air supply. The down-draft gave more uniform results than the up-draft.

The amount of air that can be passed through a bed of incandescent ore, on a porous hearth, is also surprising; as much as 14,000 cu. ft. of air per hour have been passed through a hearth 10 ft. square, continuously, without disturbing the ore particles.

The following results were obtained on tests made by the New Jersey Zinc Co. with the demonstration furnace at Denver. The furnace has a hearth area 100 sq. ft. It is arranged for hand rabbling and fired with coal. The tests were made under the supervision of W. C. Wetheril, consulting engineer and metallurgist of the Empire Zinc Co., and Wm. H. Paul, assistant engineer. The chemical determinations were made by the company's chemist, E. M. Johnson.

WITHOUT AIR (24 HOURS)

	Sulphur			
	Total S	Sol. H_2O	Sulphates Na_2CO_2	Insoluble S
11.00 a. m. Charged raw ore	34.3	0.044	0.11	34.15
1.00 p. m.—second hour	19.5	0.760	1.17	17.57
3.00 p. m.—fourth hour	17.6	0.150	0.37	17.08
5.00 p. m.—sixth hour	16.6	0.150	0.37	16.11
7.00 p. m.—eighth hour	12.8	0.130	0.39	12.28
9.00 p. m.—tenth hour	11.4	0.120	0.29	10.99
11.00 p. m.—twelfth hour	5.4	0.190	0.62	4.59
1.00 a. m.—fourteenth hour	2.9	0.110	0.56	2.23
3.00 a. m.—sixteenth hour	3.2	0.180	0.65	2.37
5.00 a. m.—eighteenth hour	2.3	0.25	0.78	1.27
7.00 a. m.—twentieth hour	1.1	0.15	0.81	0.14
9.00 a. m.—twenty-second hour	1.4	0.23	0.87	0.30
11.00 a. m.—twenty-fourth hour	2.5	0.72	0.19	0.59
Roasted ore, final average of entire charge	3.1	0.72	1.17	1.21

	SiO_2	Fe	Zn	Pb
Crude concentrates	1.6%	10.2%	46.8%	5.7%
Roasted concentrates	1.6	11.6	53.4	5.0

Weight of charge, raw, 2000 lb.
Weight of charge, roasted, 1690 lb.
Shrinkage, 310 lb.
Coal consumed (slack), 3052 lb.

WITH AIR (12 HOURS)

	Sulphur		
	Total	Soluble	Insoluble
9.45 a. m. Charged raw ore	34.3	0.11	34.5
10.45 a. m.—first hour	26.18	0.21	25.87
11.45 a. m.—second hour	21.03	0.25	20.87
12.45 p. m.—third hour	19.70	0.32	19.38
1.45 p. m.—fourth hour	17.90	0.34	17.56
2.45 p. m.—fifth hour	15.04	0.40	14.64
3.45 p. m.—eighth hour	11.61	0.42	11.19
4.45 p. m.—seventh hour	6.75	0.48	6.27
5.45 p. m.—eighth hour	3.17	0.56	2.61
6.45 p. m.—ninth hour	1.23	0.60	0.63
7.45 p. m.—tenth hour	1.12	0.63	0.49
8.45 p. m.—eleventh hour	0.85	0.66	0.19
9.45 p. m.—twelfth hour	0.68	0.50	0.18
Roasted ore, final average of entire charge	0.68	0.48	0.19

	SiO_2	Fe	Zn	Pb
Crude concentrates	1.6%	10.0%	46.9%	5.8%
Roasted concentrates	1.6	11.8	55.6	3.3

Furnace charge raw ore, weight 1800 lb.
Furnace charge roasted ore, weight 1551 lb.
Shrinkage, 249 lb.
Coal (slack) consumed, 1160 lb.

In these comparative tests, alternate charges of ore were roasted without and with air passing through the hearth, other conditions remaining the same.

From these tests it was concluded that, with the porous hearth the capacity of the furnace was increased from two and one-half to three times; that the amount of fuel required was only 35 per cent. of the amount required without the air, and that the total cost of roasting was reduced by 65 per cent.

Two mechanical furnaces, 10 ft. wide and 100 ft. long were then erected to roast this and similar material, but the lead and other ingredients of the ore formed a smooth crust due to the friction of the rabbles with the stationary ore on the hearth, which soon became impervious to the air. To what extent such a crust would form in roasting other ores is somewhat questionable. In silicious ores, like those of Cripple Creek, no crust of any kind is discernible between the moving and stationary ore of the hearth, even after furnaces have been in operation for years. The stationary ore is as permeable as the moving ore. Under such conditions no crust difficulties should arise, and the capacity of the furnace should be enormously increased, and the cost of roasting materially diminished.

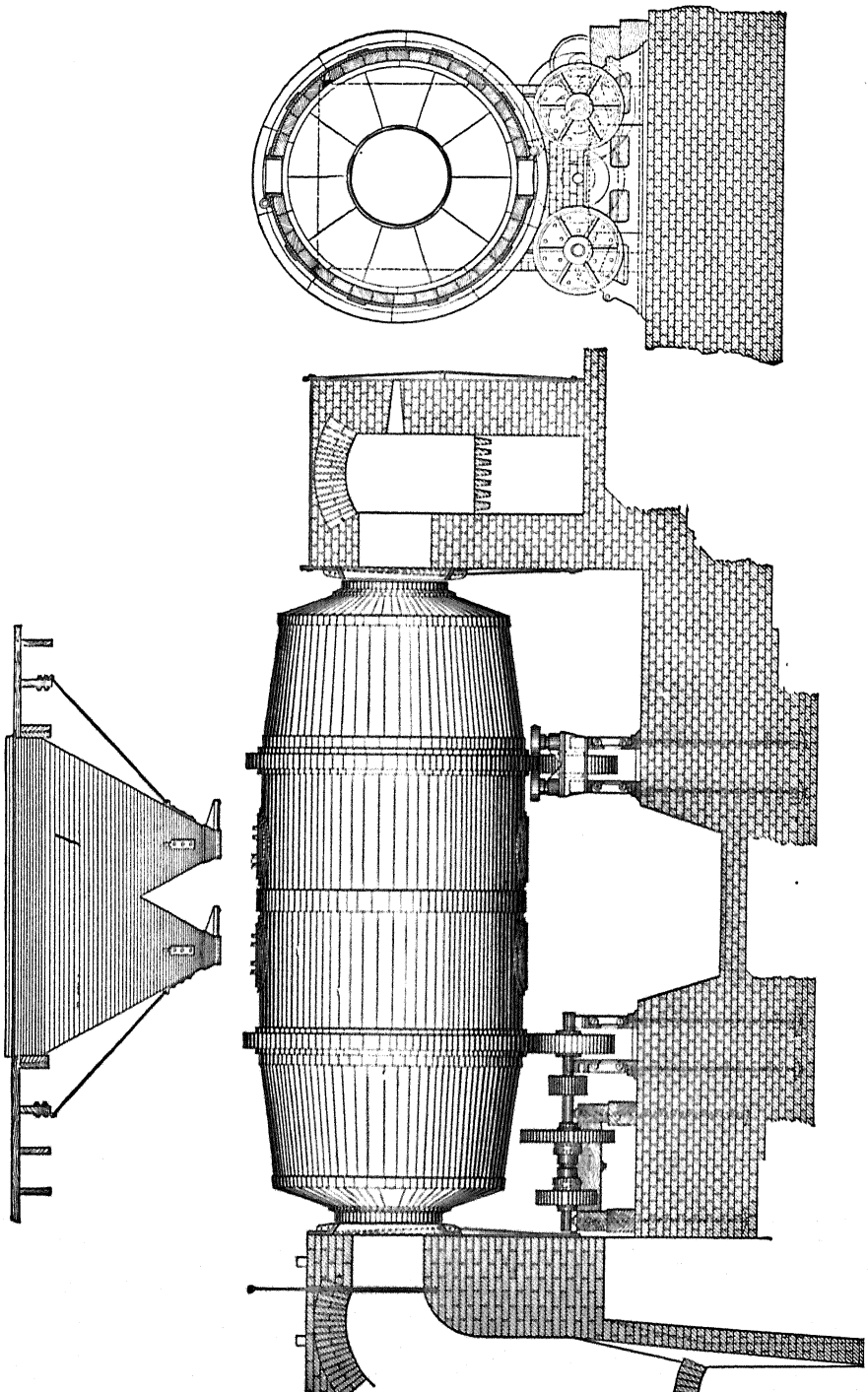


FIG. 35.—Bruckner furnace. Longitudinal and transverse sections; fixed fire-box type.

REVOLVING FURNACES

Bruckner Furnace.—The Bruckner furnace was introduced in Colorado in 1867, and since that time has been more or less generally used both in oxidizing and chloridizing roasting.

The furnace, as shown in Figs. 35 and 36, consists of a cylindrical shell of steel plate, with circular openings at each end. Two circular tracks are fastened around the cylinder, at equal distances from the ends. With these tracks the cylinder rests on four riding wheels or rollers, which are mounted on strong cast iron frames. Two of the rollers have double flanges to keep the cylinder in proper alignment.

A revolving motion is given the cylinder by means of cogs and pinions, so adjusted that the proper reduction in speed is made between the driving pulley and the revolving cylinder. A large peripheral cog is fastened to the cylinder, which meshes into a pinion of suitable size. Fig. 36 shows the mechanical details of the cylinder and driving mechanism for a furnace 8 1/2 ft. diam. by 18 1/2 ft. long, and having a capacity of 8 to 11 tons of ore at a charge.

A fire-box is placed at one end of the cylinder, the throat of which corresponds with the central end opening; while a similar opening at the other end communicates with the stationary flue or dust chamber. The fire-box for the furnace is built of brick, and in some instances it is mounted upon wheels so that it may be removed to facilitate the relining of the shell. When a complete roast is desired, a stationary fire-box is to be preferred over a removable one.

There are four doors in the cylinder; two of these are placed diametrically opposite the other two. The doors serve for charging and discharging the ore. A hopper is placed above the furnace large enough to hold a charge of the material to be roasted; this hopper has two outlet spouts, each provided with a slide, which corresponds with the furnace doors.

The shell, as well as the ends, are lined with brick. Provision is made in the driving mechanism to regulate the speed from one revolution per minute to one revolution in 3 minutes.

The ends of the cylinder are sometimes contracted to facilitate discharging of the ore, but this is not necessary, except for large furnaces.

These furnaces are usually built of various standard sizes; the dimensions, weights, and capacities, are approximately as follows:

BRUCKNER ROASTING FURNACES

Size of furnace	Weight of iron work	Number fire brick	Number common brick	Capacity, per charge, tons
6 ×12	17,800 lb.	1,300	18,000	4
7 ×18	30,000 lb.	1,700	20,000	6 to 8
8 1/2×18 1/2	52,000 lb.	2,800	25,000	8 to 11
8 1/2×28	69,000 lb.	3,300	27,000	15 to 25

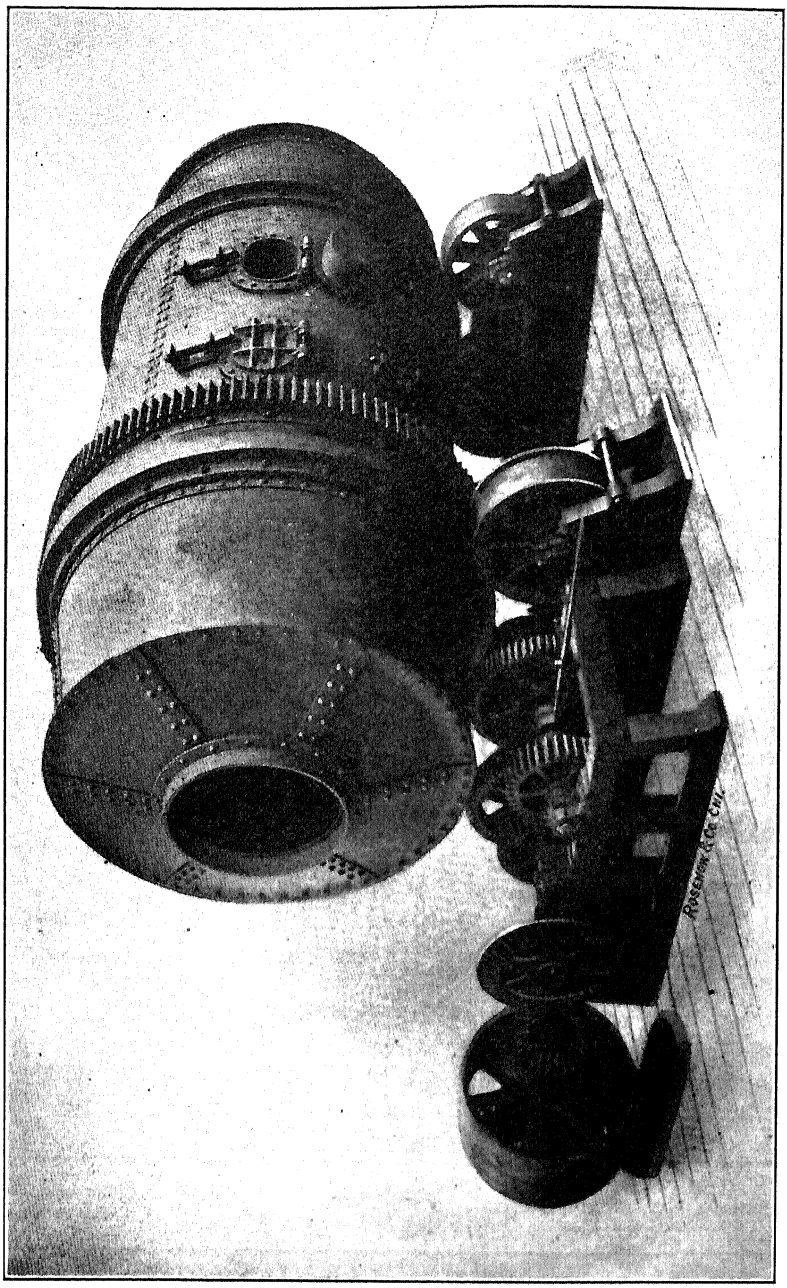


FIG. 36.—Bruckner furnace. Perspective view, showing mechanical details.

In the operation of the furnace two of the doors in the cylinder are opened and brought directly under the hopper spouts. The slides are then withdrawn and the charge allowed to run in. The furnace is then given a slight turn to bring it in a convenient position to close the doors, which are then fastened as tight as possible.

The cylinder is then revolved and a strong fire maintained, until the sulphur is well ignited. If the charge being roasted is heavy sulphide ore or pyritic concentrates, the firing is discontinued after the sulphur is thoroughly ignited. The heat developed by the burning sulphur is considerable, and if augumented by external firing, caking and balling of the ore would take place.

Usually two charges of ore are roasted in 24 hours. If the ore is a heavy sulphide, the furnace can be run from three to four hours without firing. If the ore is being chloridized, salt is then added, and the roasting continued with a moderate fire. The temperature may be observed, and scoop samples taken, from a hole back of the flue. When the roasting has fairly well progressed, the charge in the furnace loses its tendency to run like a liquid, and assumes an inclined position, up to 45 degrees. This unequally distributed weight acts against the direction of the motion, and if the clutch is thrown out in order to stop the furnace, this weight will pull the furnace back nearly a quarter of a turn. If the ore is given a chloridizing roast, the salt is introduced through two of the doors and well scattered over the charge.

When the roasting is finished two cars are pushed under the furnace, one for each door. All four doors are then opened and the furnace again revolved. The receiving cars are made narrow so that no ore is dropped beyond the confines of the car, because the ore discharges through the doors over a large arc.

The revolving motion of the Bruckner furnace should be slow. The ore, in any case, is continuously changing its position and exposing new surfaces. There is no advantage in moving the ore more rapidly than the ore at the surface can be oxidized. One revolution in two or three minutes should be ample.

In the larger sized Bruckner furnaces, the ore is exposed to rather an uneven heat. That near the fire-box is at a considerably higher temperature than the ore at the further end, from 18 to 28 ft. distant. To overcome this defect, O. Hofmann modified the Bruckner furnace by placing a fire-box at both ends, and arranged so that the fire-boxes could be used intermittently, by damper arrangements connecting with the flue, or dust chamber.

The cylinders are made to revolve slowly; the smaller ones by applying power to a shaft carrying the friction rollers, the larger ones by a pinion which engages a spur gear surrounding the cylinder.

Howell-White Furnace.—The Howell-White furnace, Figs. 37 and 38,

consists essentially of a long telescope-shaped cast-iron cylinder, made in sections with cast flanges, carefully fitted, and bolted together. The cylinder is supported on a system of rings resting on friction wheels, and guided in a central position by rollers in upright frames, and revolved by friction of the wheels operated by gears and pulleys. The flame passes through the revolving cylinder from a fire-box at one end to the flue at the other.

That one-third portion of the cylinder nearest the fire has a larger external diameter than the part next the flue, but it is lined with fire brick to make its internal diameter the same as that of the smaller part, which, although unlined, stands the heat very well. In some instances the entire cylinder is lined, and this is probably the best when the ore is given a thorough oxidizing roast.

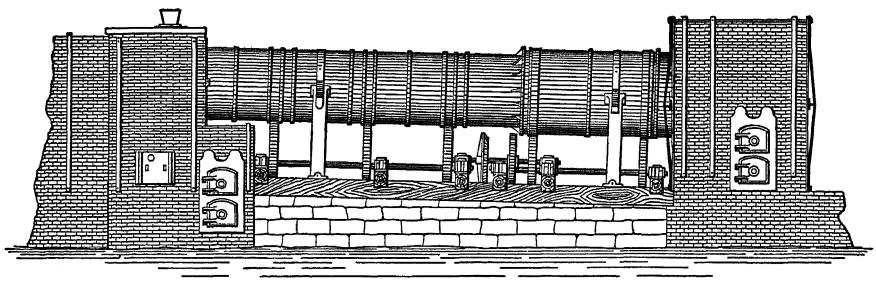


FIG. 37.—Howel-White furnace.

Projecting fire brick, arranged spirally in the brick-lined portion, assist in oxidation by raising and showering the ore through the flame, which passes directly through the cylinder. When the feed end of the furnace is not lined with brick cast-iron projections are provided for the same purpose. These projections make large quantities of dust, sometimes from 30 to 50 per cent. of the ore charged, and for that reason are frequently omitted.

The cylinder is inclined slightly toward the discharge end in order to advance the ore gradually against a constantly increasing temperature. The furnace is fed at the upper end with dry ore by means of a screw feeder, and then makes its way automatically toward the lower end of the furnace, where it passes out, dropping between the end of the cylinder and the fire-box, into the vault.

On account of the excessive dust from the furnace, an auxiliary fire-box is usually placed at the flue end of the furnace for roasting the flue dust as it passes, suspended in the air, into the dust chamber. If the spiral projections are omitted from the cylinder, the auxiliary fire to roast the dust may also be omitted. The ore as fed into the furnace has its sulphur fairly well eliminated before it comes against the more or less direct flame from the fire.

The furnace requires very little repair, and very little power to run it, while its capacity is quite large. The revolving speed of the furnace is adjustable; and may vary from three to eight revolutions per minute, the larger furnaces revolving more slowly than the smaller ones.

Fig. 37 shows a longitudinal elevation of the furnace and Fig. 38, a section through the discharge end.

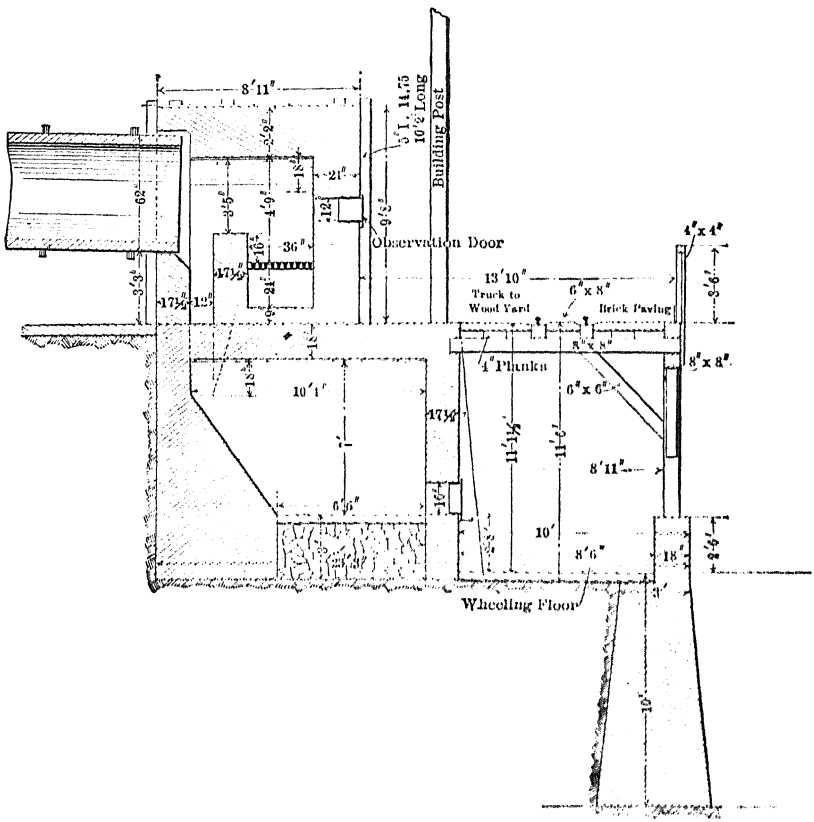


FIG. 38.—Howell-White furnace. Discharge end and ore vault.

The following table gives the standard sizes of the Howell-White furnace, with weights, material, capacities, etc.

HOWELL-WHITE ROASTERS

Diameter inches	Length, feet	Capacity in tons	Weight of iron work, lb.	Fire brick required	Common brick required
31×41	23	15 to 20	25,000	1,900	22,000
52×62	27	30 to 50	43,500	2,700	28,000
52×62	34	50 to 60	54,000	2,700	28,000
52×62	36	60 to 70	59,000	3,000	31,000

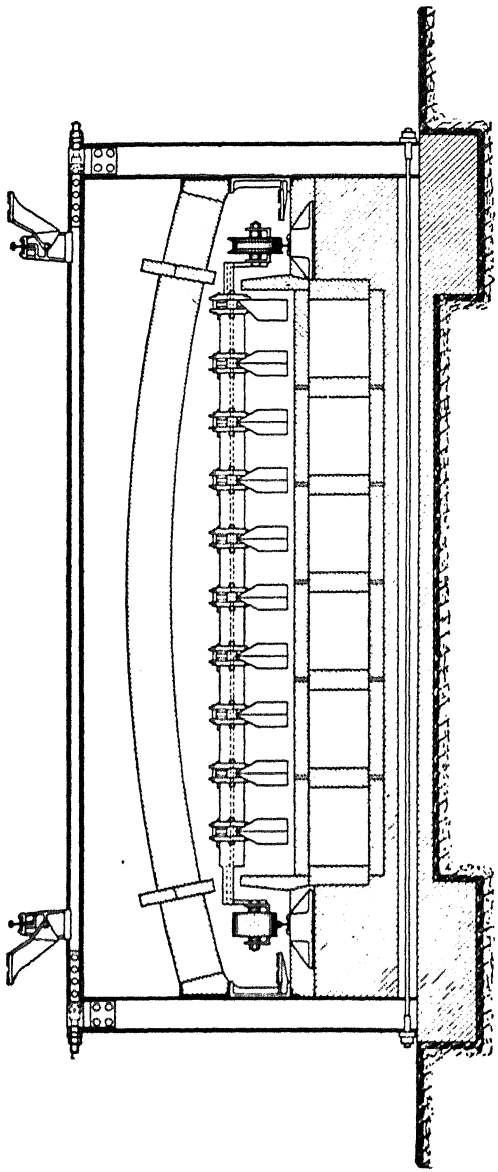


FIG. 39.—Brown muffle furnace. Transverse section.

This furnace has been largely used for chloridizing roasting; when so used the salt must be fed in with the ore. A portion of the salt may be added as the ore drops into the vault, after passing through the cylinder.

Muffle Furnaces.—All of the well-known designs of standard reverberatories may be modified to muffle furnaces by placing flues under the hearth, and by having two concentric arches over the reverberatory chamber.

A modification of the hand reverberatory for muffle roasting, in chloridizing pyritic cinders, is shown in Fig. 49, page 263.

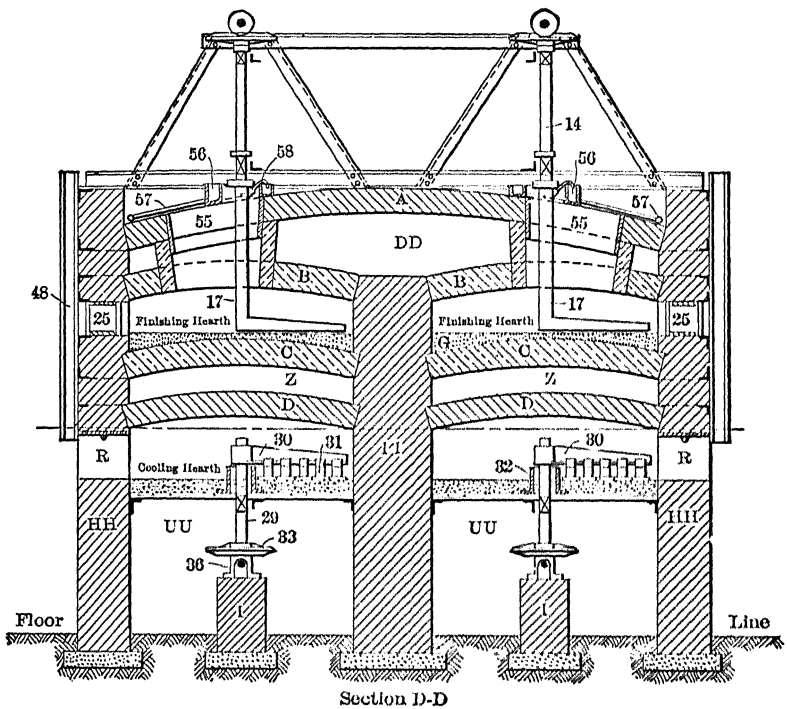


FIG. 40.—Edwards muffle furnace. Transverse section.

A modification of the Brown furnace for muffle roasting is shown in Fig. 39; for the Edwards, in Fig. 40; for the Wedge, in Fig. 41, and for the Allis-Chalmers McDougal, in Fig. 42. These illustrations fairly represent the modifications required for the straight line chain-driven roasters; the straight line circular rabbled roasters, and the multiple hearth furnaces with central revolving shaft.

Muffle furnaces are not as economical as reverberatories, but for certain work present recognized advantages. The heat can be regulated more uniformly and the amount of dust is minimized. In chloridizing

roasting, muffle furnaces present the decided advantage that the volatile metals in the fumes can be more readily condensed and recovered. In reverberatories, or other direct-fired furnaces, the gases from the fires are mixed with those from the ore, so that the volume of gases passing through the condensers for the recovery of the volatilized values is quite large, and by far the largest amount of air in such cases is due to the combustion of the fuel. In chloridizing roasting only that part of the furnace containing the ore after the salt is added need be muffled.

A combination of reverberatory and muffle can frequently be used to advantage to avoid excessive dust loss, and where it is intended to make

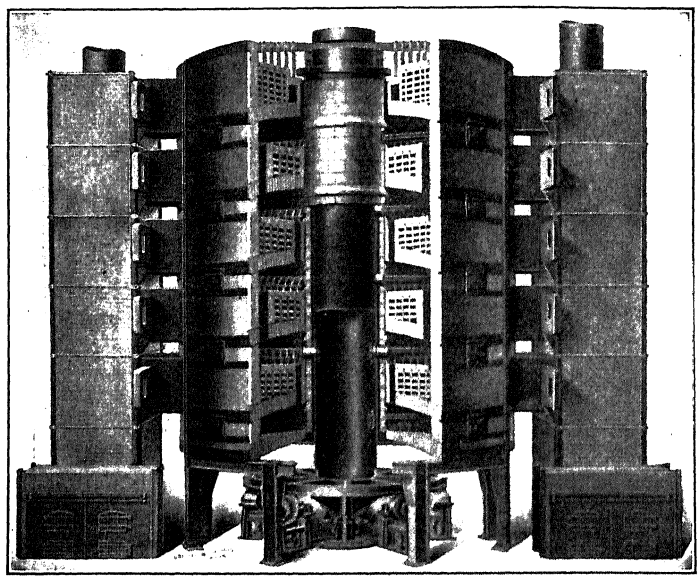


FIG. 41.—Wedge muffle furnace.

sulphuric acid to leach the copper from the roasted ore. Fig. 42 shows such a furnace, in which the three lower hearths are muffled with special tile to keep the products of combustion from the fire-boxes separate from the sulphur dioxide gases; the furnace is equipped with uptakes for conveying the gases, and a separate stack is arranged with connections to the muffles for taking away the gases of combustion. If sulphuric acid is to be made, furnaces may be muffled so as to get the maximum sulphur dioxide content in the furnace gases for the manufacture of the acid, and the remaining sulphur in the ore can then be eliminated by a continuation of the same hearth into a reverberatory chamber in which the fumes from the ore and from the fuel commingle and pass out together, and separately from the sulphur gases from the muffle.

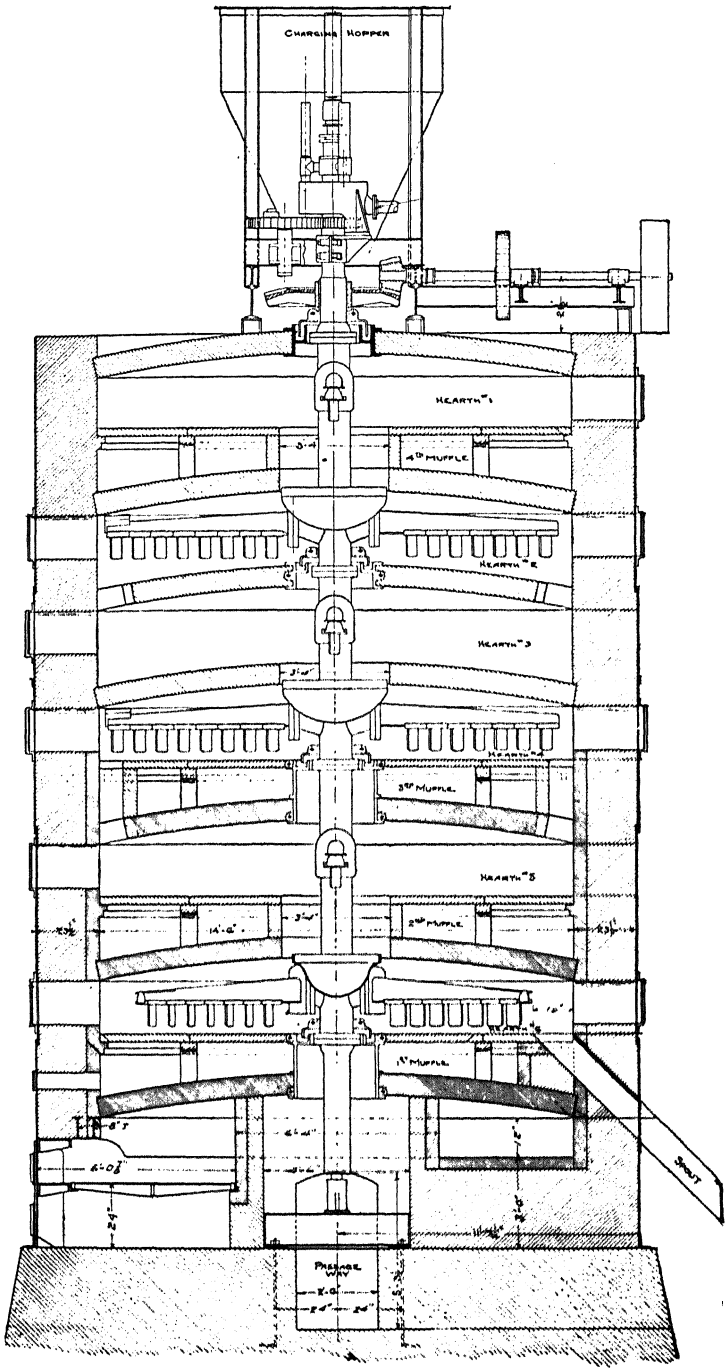


FIG. 42.—Allis-Chalmers McDougal muffle furnace.

Fig. 41 shows a muffle furnace now largely used in the chloridizing roasting of cupriferous pyritic cinders for the extraction of the copper. This type of furnace is replacing the hand muffle furnaces used for that purpose.

Ore Coolers.—After roasting, it is necessary to cool the ore before charging it into vats or agitators for chemical treatment. The cooling in almost all of the furnaces is done in combination with the roasting by a mechanical device similar to the rabbling mechanism of the furnace. Usually, as in the case of the Pearce, Holthoff-Wethey, and Wedge furnaces, by dropping the ore to a lower open hearth and continuing the rabbling as in the roasting. Frequently the cooling hearth is made of water jackets, or pipes, through which cold water is continually circulated. When the design does not conveniently lend itself to the use of a lower hearth, the ore is cooled by a rabbling device similar to the roasting mechanism, and either connected with it, or as a separate apparatus. A push conveyor, with water jacketed bottom, arranged to deliver the cooled ore to the leaching plant, makes a good cooler. In Figs. 20 and 22 the lower hearth of the furnace is used to cool the ore.

Dust.—Dust presents one of the most serious problems in roasting. If the ore fed into a furnace contains an excessive amount of dust, the capacity is reduced. In one of the Cripple Creek mills, when the ore in the supply bins became low and contained an excessive accumulation of dust, the capacity of the furnaces was reduced from 100 to 90 tons per day, but this decreased capacity was of short duration, as the bins soon became empty and a fresh supply of ore had to be provided. Ore crushed exceedingly fine cannot be roasted at the same rate as ore crushed from 8 to 20 mesh.

All furnaces make more or less dust in roasting, which if not recovered, represents a serious loss; and if recovered, an additional expense. A dust chamber is usually a necessary adjunct to a roasting furnace, and must be taken into account in a roasting installation.

For straight line reverberatory furnaces the dust recovered in suitable dust chambers varies from 1.5 to 3.5 per cent. of the ore roasted. Much depends on the nature of the ore and the speed of travel of the reverberatory gases. In multiple hearth furnaces the recovery in the dust chambers will usually be from 3.5 to 5 per cent. in careful work. In revolving furnaces, the dust recovery in the flues or chamber is quite large.

M. W. von Bernewitz gives as an example[1] a battery of six roasting furnaces with a capacity of 20 tons each of Kalgoorlie ore daily, that has been crushed to 25-mesh screen. These furnaces are connected with a flue $100 \times 7 \times 7$ ft. and a stack 100×6 ft. with a 1/2-in. draft. Twenty tons of flue dust are collected monthly, which amounts to about 3.5 per cent. of the ore roasted.

[1] *E. and M. J.*, Feb. 26, 1910.

As a rule the dust collected from the dust chambers is not well roasted. This is largely due to the fact that the partially heated ore dusts more than after it has been heated to incandescence, but more largely due to the rapid travel of the fuel and furnace gases over the partially heated ore at the rear of the furnace. Roasting furnaces, as usually built, exhaust all the gases from one opening at the rear of the furnace, so that as each fire-box discharges its gases into the roasting chamber, the draft, or speed of travel of the gases against the roasting ore must be proportionately increased with each addition. At the rear of the furnace all the fire-boxes have poured their gases into the roasting chamber, and as the ore is rabbled, the rapid movement of the gases over it, whip a large proportion of the finer unroasted material into the dust chamber.

There is no reliable data available on the dust loss through the stacks. It is probably more than usually supposed. In one of the Cripple Creek mills there was at one time an unaccountable loss of values amounting to 1 per cent. It was thought that much of this was due to dust losses in the furnace stack.

CHAPTER VII

TYPICAL EXAMPLES OF ROASTING

Roasting of Cripple Creek Ores.—Most of the ores in Cripple Creek are roasted before chemical treatment. The amount roasted per day is about 1500 tons. The ore after roasting is treated both by the chlorination and cyanide processes. All the furnaces now in use are designed to roast 100 tons of ore daily. Of the furnaces in regular operation, there are three Pearce furnaces; six Holthoff-Wethey; eight Edwards, and one Holthoff revolving hearth. All of these furnaces are giving satisfactory results.

The average chemical composition of Cripple Creek ores which are roasted, is about as follows:

SiO_2,	60 to 70 per cent.	S,	1.5 to 3.0 per cent.
Al_2O_3,	18 to 22 per cent.	Pb,	trace to 0.10 per cent.
CaO,	1.5 to 2.5 per cent.	Zn,	trace to 0.10 per cent.
MgO,	0.1 to 0.25 per cent.	Mn,	trace to 0.15 per cent.
BaO,	trace to 0.25 per cent.	K and Na,	5.0 to 10.0 per cent.
Fe,	3.0 to 7.0 per cent.	Te,	trace.
		Cu,	trace.

The ore as it comes from the mines is crushed through rock breakers and rolls to pass through 8- to 16-mesh screens. The oxidized ore, as it comes from the mines, contains as low as 0.25 per cent. sulphur; the unoxidized, from the deeper levels, contains as much as 5 per cent.; the average for the different mills ranges between 1.5 and 2.75, depending on the condition of the mines from which most of the ore comes.

Ore low in sulphur—from 1.0 to 2.0 per cent.—is roasted until it contains between 0.25 and 0.60 per cent.; that carrying from 2.25 to 3.25 per cent. to between 0.50 and 0.85 per cent. All of the mills are at present equipped with furnaces which regularly roast 100 tons of ore containing from 1.5 to 2.5 per cent. sulphur; when the sulphur exceeds 2.5 per cent. the capacity is likely to be reduced to 90 tons, while on the contrary, if the sulphur is about 1.5 per cent. or less, the capacity may exceed 120 tons per day of 24 hours. The hearth area of these furnaces is between 1200 and 1500 sq. ft.; the grate area about 75 sq. ft.

Many of the furnaces are fired with producer gas. The ore coolers are usually located directly under the roasting hearths and form part of the furnace, so that the ore on issuing from the roasting hearth drops to the cooling hearth, to be turned over, cooled, and advanced by the cooling hearth rabbles.

The consumption of fuel varies from 10 to 15 tons of Western bituminous coal per 100 tons of ore roasted. Lignite is used to some extent, but is not as effective as the longer flame bituminous. Oil and residuum are also used, but in connection with coal. If they are used together it takes 5 tons of coal and 150 gallons of oil per 100 tons of ore.

The ore, in roasting, is given an initial temperature at the first fire-box of 1200 to 1300° F. and at the last fire-box from 1400 to 1500° F. The temperature of the fuel gases entering the reverberatory chamber is approximately 1800° F. The ore never attains this temperature, because it is being continually stirred and advanced, so that only the top layer is momentarily exposed to the higher temperatures.

The charge remains in the roasting furnaces from 2.5 to 3.0 hours, and on the cooling hearth from 1.5 to 2.5 hours. The bed is from 2.5 to 3.5 in. thick. In some of the furnaces the ore is rabbled every 17 seconds; in others every 35 seconds.

One man attends a furnace; he usually has a helper to wheel the coal and ashes. One such helper attends several furnaces.

The cost of roasting ranges from 45 to 55 cents per ton, estimated approximately as follows, per 100 tons:

Coal, 12 tons, at $2.00 per ton,	$24.00
Three furnacemen, 8-hour shifts, at $2.50,	7.50
Coal and ash trammer,	2.25
General repairs, oil, water, etc.,	5.00
Power,	5.00
Interest on investment, at 6 per cent.,	3.50
Cost per 100 tons,	$47.25
Cost per ton,	0.4725

To this must be added the proportional share of administration, etc., which will bring the cost per ton about 50 cents. These estimates include cooling and conveying.

The furnaces do not give much trouble. It is not unusual to have a 100-ton furnace in continuous operation for months without a serious shut-down and no appreciable repairs; with occasional changing of the rabbles the roasting proceeds indefinitely.

The accumulation of the dust in the dust chambers is usually from 1.5 to 2.5 per cent.; in some mills it is re-treated with the ore, while in others it is shipped to the smelters, after briquetting. The dust is not well roasted, and contains much undecomposed pyrites, and is high in soluble sulphates. When the dust is treated in the mills, it is automatically again fed, with the ore, into the furnaces, and in this way worked up with regular charges.

The average value of the dust is higher than that of the ore; this is doubtless due to the fact that in crushing, the sulphides and tellurides

are pulverized more than the quartz. There has not been any appreciable loss found by volatilization in oxidizing roasting.

Roasting Arsenical Sulphide Ore at the Golden Gate Mill, Mercur, Utah.—The ore contains about 5 per cent. sulphur, and from 4 to 6 per cent. arsenic, and small quantities of lead and copper. It is crushed to 10 mesh, when it is delivered to the roasters. The gold in the ore is found in minute cleavage planes and crevices, and is easily attacked by the cyanide solution; for this reason, crushing to 10 mesh is required only for the sake of quick and complete roasting, and not for the purpose of facilitating the leaching.

The plant consists of four coal-fired roasters, 125 ft. long by 12 1/2 ft. wide. Each furnace consists of a single roasting hearth, whose roof serves as a cooling hearth. The ore is fed into the lower level, and is moved continuously in one direction by travelling rabbles. Escaping from the end, it is elevated to the upper hearth, where it again travels the length of the furnace, exposed to the air.

The ore occupies about four hours in roasting, and the same length of time in cooling. Its volatile components are reduced from 5 per cent. sulphur, and 4 to 6 per cent. arsenic, in the raw state, to 0.6 per cent. sulphur and 0.8 per cent. arsenic in the roasted ore.

During the year ending June 30, 1906, four roasters were in operation for 46 days, five roasters for 237 days, and six roasters for 82 days. The total number of roaster days was, therefore, 1861. As 126,358 tons of sulphide ore were roasted, the average work was 68 tons per roaster per day. The operation costs, including maintenance and repairs, for the year 1906 were as follows:

	Total	Per ton
Coal,	$73,759	$0.583
Labor,	33,736	0.267
Power and other items,	18,544	0.146
	$126,039	$0.998

Slack coal is burned which costs $5.25 delivered. The labor consists largely of firemen who receive $2.75 for eight hours.[1]

Roasting of Casilas Concentrates, Victoria, Australia.[2]—The following is an average analysis of the concentrate: Lead, 4.48 per cent.; zinc, 5.26 per cent.; iron, 31.65 per cent.; arsenic, 15.16 per cent.; sulphur 31.63 per cent.; unestimated, 11.91 per cent.; the copper rarely exceeded 1 or 2 per cent. It was usual to make from 15 to 20 per cent. concentrate, running from 3 to 4 oz. of gold, and containing over 50 per cent. of the total gold value of the ore crushed. The tailings from the stamp battery and concentration tables are cyanided, and the concentrate chlorinated.

[1] *E. and M. J.*, Nov. 10, 1906.

It was found that short hand-rabbled reverberatories were unsuited for roasting the concentrate on account of the charge fusing too easily. As the galena could not all be separated, some form of mechanical furnace was necessary, and two Edwards' mechanical furnaces with 60-ft. hearths were installed. One man per shift of 8 hours, attended to all the work of the two furnaces, with a weekly capacity of 30 to 35 tons each. The furnace man charged the hoppers, stoked the two furnaces, and looked after the engine and dynamo for lighting the works. The fume was lead into a brick flue 300 ft. long and 5 ft. by 4. ft. inside, with a 40-ft. iron stack 2 1/2 ft. in diameter.

The height of the top of the stack above the hearth of the furnaces was 70 ft.; small dust chambers were built between the ends of the furnace and the flue. The iron stack did not suffer at all, and acted as an excellent arsenic condenser. It was necessary to clean the whole length of the flue every three months; about 30 tons of deposit being obtained.

The flue dust for the first 100 ft. consisted partially of roasted concentrate and arsenic soot, assaying about 3 oz. in gold per ton, or about the same value as the concentrate roasted. The last 200 ft. of the flue contained arsenic soot comparatively free from concentrate, and assayed 7 1/2 dwt. The arsenic at the base of the stack had to be cleared out weekly.

Just before the finish of the roast, 1 to 1 1/2 per cent. salt was added to the concentrate in order to obtain a sweet roast. No evidence of loss of gold by volatilization could be obtained.

The roasted ore discharged into a push conveyor which carried the ore to a steel bucket elevator; this took it to a cooling bin over the treatment vats. Dry wood was used as fuel; any green sticks getting in generally had the effect of throwing back the charge to magnetic oxide. Badly roasted ore set hard in the vats, while roasted ore did not. The ore in the hand-rabbled furnaces always roasted black; while in the mechanical furnaces, it roasted chocolate color, but never bright red. The brighter the color obtained in roasting, the better the roast; although the magnet failed to show any difference. Practically no zinc was sent to the flue, the heat not being high enough; it was in the roasted ore mostly as sulphate or basic sulphate.

During the chlorination treatment, the zinc was almost all leached out by the sulphuric acid, but the amount of zinc seemed to have no influence on the extraction, other than to prolong the period, through packing of the charge in the vats as the zinc leached out. The chlorine solution used had a strength of 0.09 to 1.2 per cent. of chlorine, and from 0.5 to 1 per cent. sulphuric acid, over and above the amount required to combine with the beaching powder. The copper gave very little trouble.

An extraction of 85 per cent. was obtained on well-roasted ore, the loss amounting to 1 to 2 dwt. per ton crushed. Numerous experiments

were carried out to try and better the extraction, but with no success, although they led to a steady decrease of the cost of chemicals. Fine grinding after roasting gave no better results. The cost of roasting the concentrate at the rate of 54 tons per week, was as follows:

Wages,	$0.946
Fuel,	1.066
Repairs,	0.040
General charges,	0.446
Cost per ton roasted,	$2.498

Notwithstanding the extremely refractory nature of the concentrate, over 50 per cent. was saved by roasting and chlorinating, over the cost of shipping to the smelters. The concentrate sometimes carried as high as 20 per cent. zinc.

Roasting at Kalgoorlie.[1]—The ore is crushed dry in Krupp ball or Griffin mills and roasted in Edwards or Merton furnaces. At the Kalgurli mine the nine No. 5 Krupp mills, eight of which are in continuous use, are capable of putting through between 10,000 and 11,000 tons per month. These mills maintain a duty of 45 tons per 24 hours when crushing through a 37-mesh screen. The load of balls weighs about 2300 lb.; one 18-lb. ball is added every day to compensate for wear and tear. The mills run at 25 r. p. m. and require, including their share of counter-shaft friction and dust fans, 25 h. p. The cost for crushing through 37-mesh screen at the South Kalgurli is 79 cents per ton; the cost at the Associated and Associated Northern, crushing through 27-mesh screen in ball mills, is 59 cents.

The following table gives the essential facts for roasting at the Kalgoorlie mines:

ROASTING FURNACES AT KALGOORLIE MINES

Mine	Type of furnace	Area of hearth	Average tonnage (24 hours)	Sulphur in ore per cent.	Fuel consumption per cent. (wood)	Cost per ton
Associated Northern	Merton....	630 sq. ft.	23	5.0	12.2	61.0¢
Kalgurli	Edwards...	70×9 ft. 6 in.	23	4.2	13.0	68.4¢
Kalgurli	Edwards...	63×9 ft. 0 in.	22	4.2	13.0	
Perseverence	Edwards...	121×13 ft. 6 in.	93	4.0	11.0	65.8¢
Great Boulder	Edwards...	64×6 ft. 6 in.	25	3.5	9.2	59.2¢
Great Boulder	Merton....	422 sq. ft.	25	3.5	9.2	59.2¢
South Kalgurli	Merton....	617 sq. ft.	36	3.8	10.6	64.0¢
Associated	Merton....	445 sq. ft.	20	6.1	10.0	63.0¢

Fuel represents about 50 per cent. of the total roasting costs.

[1]Gerard W. Williams, *E. and M. J.* Feb. 15, 1908.

Recently[1] at the Associated, the smaller Merton furnaces have been replaced by the larger sized Edwards furnaces. The sulphur in the ore averages about 5.5 per cent. The ore gets a dull red heat about the fifth rabble from the end. The furnaces average about 95 tons per day each. They are motor driven, and use 6 amperes at 550 volts each (4.4 h. p.). The end fire-boxes are not used much, just two or three logs are kept burning to warm the air passing through the fire-bars. The middle fire-boxes are fired heavily, and the sulphur continues to burn till the fourth rabble from the discharge, namely 22 ft. from the end, and then discharges quite cool. Fuel consumption averages 11 per cent. of the roasted ore. The flue temperature is 700° F. One man attends two furnaces. The roasting cost is 60 cents per ton. About 81,000 tons of ore and concentrate are roasted at Kalgoorlie monthly.

[1] M. W. von Bernewitz, *Mining and Scientific Press*, May 13, 1911.

PART II

HYDROMETALLURGICAL PROCESSES

CHAPTER VIII

PROPERTIES AND SOLUBILITIES OF COPPER

Copper.—Atomic weight, 63.6; specific gravity, 8.94. Weight per cubic foot: cast copper, 542 lb.; rolled copper, 555 lb. Weight per cu. in., 0.32 lb. Copper occurs chemically as cuprous compounds, formula CuA^{I}, or cupric compounds, formula CuA^{II}, where A^{I} is a univalent or monad acid radical, and A^{II} a bivalent or dyad acid radical. As a monad atom, copper has a chemical equivalent of 63.6, as a dyad element 31.8. The amounts of copper dissolved into or deposited from a cupric or cuprous salt are proportional to the chemical equivalent of copper in these two states and to the amperes flowing. Assuming that one ampere liberates electrolytically 0.00001036 grm. of hydrogen per second, the amount of copper deposited by the passage of one ampere will be as follows:

	Cuprous compounds	Cupric compounds
One ampere per second	0.0006589 grm.	0.0003295 grm.
One ampere per minute	0.03953 grm.	0.01977 grm.
One ampere per hour	2.372 grm.	1.186 grm.
One ampere per day	56.93 grm.	28.46 grm.
One ampere per year	20.78 kilogrm.	10.39 kilogrm.

The melting-point of copper is 1080° C. It is a red metal, but thin sheets transmit a greenish-blue light, and it also shows the same greenish-blue tint when in a molten condition. Of the metals in ordinary use, only gold and silver exceed it in malleability. In ductility it is inferior to iron and cannot be so readily drawn into exceedingly fine wire. Although it ranks next to iron in tenacity, its wire bears only about half the weight which an iron wire of the same size would support. As a conductor of heat it is surpassed only by gold. Next to silver it is the best conductor of electricity.

Dry air has no action upon it; in moist air it becomes coated with a film of oxide which protects it from further action of air or of water. It forms a number of very important alloys with other metals; with tin it forms bronze; with zinc and sometimes with small amounts of lead and tin, it forms brass; and with nickel and zinc it forms German silver.

Copper which has become hardened by mechanical work may be again made malleable by heating. The boiling-point of copper is about 2000° C. Molten copper has a great tendency to dissolve hydrogen, carbonic oxide, and sulphur dioxide, which it evolves again on solidifying. Aluminum, cobalt, nickel, zinc, cadmium, tungsten, molybdenum and iron, are more or less readily dissolved by it, as also are cuprous oxide, sulphide, and phosphide, and the arsenides, arsenates, antimonides and antimonates.

On heating copper to a low red heat, far below its melting point, it becomes covered with a film or scale which consists of a mixture of the cuprous and cupric oxides.

Copper exhibits a greater affinity for sulphur than do any of the other metals. It also unites directly with the metalloids, excepting hydrogen, nitrogen, and carbon.

The best solvents for copper are nitric acid, concentrated sulphuric acid, and aqua regia. Hydrochloric acid and dilute sulphuric acid only dissolve the metal when air or some other oxidizing substance is present; under these conditions it is more readily soluble in dilute hydrochloric acid than in dilute sulphuric acid.

Cupric chloride acts on metallic copper to produce cuprous chloride: $Cu + CuCl_2 = 2CuCl$.

Cuprous oxide has the property of mixing with molten copper in all proportions. Small amounts of cuprous oxide have no injurious effect upon it, but large quantities make it cold-short, and when a certain limit is exceeded, also red-short. Copper containing about 2 per cent. cuprous oxide is still as fit for ordinary use as ordinary cast-refined copper.

Cathode copper is exceedingly pure, usually about 99.93 per cent. copper, with hydrogen as the chief impurity. Objectionable cathode impurities are of two classes—those which depress the electrical conductivity and those which make the metal brittle. Arsenic and antimony represent the first class; tellurium and lead the second. Good cathode copper should show but a few thousandths of a per cent. of arsenic and antimony. Experiments have indicated that it takes but 0.0013 per cent. of arsenic or 0.0071 per cent. of antimony to lower the conductivity 1 per cent. Any conductivity troubles in electrolytic copper can almost invariably be traced to the presence of undue amounts of one or both of these elements. Impurities of the brittle-making class are rarely met with, and if present are due to mechanical contamination of the cathode, either in the bath or in the subsequent furnace treatment.

Influence of Impurities on the Properties of Copper.

Arsenic and Antimony.—Hampe, in 1892, found that 0.5 per cent. arsenic produces no bad results and that even when the percentage was

increased to 1 per cent. only a slight degree of red-shortness, but no cold-shortness could be noticed. He found that copper with 0.8 per cent. arsenic could be drawn into the finest wire. Stahl, in 1886, stated that a small percentage of arsenic prevents copper from becoming porous. Hiorns, in 1906, showed that copper with arsenic up to 0.4 per cent. was very malleable when cold; that with 0.2 per cent. each of arsenic and antimony, the same is true; and that arsenic in the presence of antimony makes the copper more malleable than it is with antimony alone, though antimony when not above 0.2 per cent. only slightly impairs the malleability of copper. He adds that arsenic in copper is highly beneficial because it deoxidizes cuprous oxide, which tends to destroy the malleability of copper. Johnson, in 1906, stated that cast copper with 0.5 per

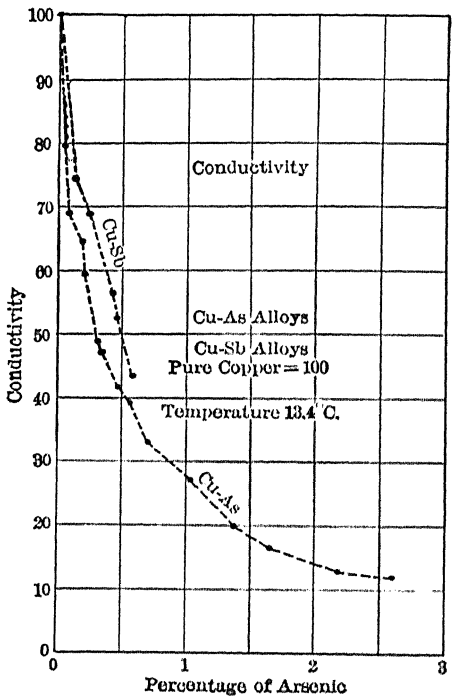


FIG. 43.—Conductivity diagram of pure electrolytic copper with arsenic and antimony as alloys.

cent. arsenic has a tensile strength of 10 long tons per square inch, and a 24 per cent. elongation. After forging, the tensile strength was raised to 12.75 tons, and the elongation to 35 per cent. Upon rolling, the tensile strength became 14 tons and the elongation 48 per cent.; and finally upon being highly wrought and cold drawn, the tensile strength of the same cast copper was raised to 15.9 tons, and the elongation varied

from 24 to 50 per cent. while the specific gravity was increased from 8.83 for copper in the cast state to 8.866 when the metal was wrought.

H. S. Hiorns and S. Lamb[1] prepared alloys consisting of pure electrolytic copper and arsenic and antimony in quantities varying from 0.05 to 3.5 per cent. These alloys were drawn into wires 0.0325 in. in diameter, and were tested for conductivity, shown by Fig. 43.

A. H. Hiorns found that with between 0.5 and 1 per cent. of arsenic the malleability seemed to diminish, but with over 1 per cent. and up to 2 and 3 per cent. arsenic, the copper rolled perfectly and was harder than pure copper. With less than 0.5 per cent., arsenic the copper should be less malleable when cooled slowly than when cooled quickly. With a certain small quantity of arsenic introduced into copper the first small portions appear to act by reducing the cuprous oxide, the remainder retaining the metallic form and toughening the copper.

Arsenic invariably improves the forging properties where added to impure copper. Arsenical copper is largely specified for in materials, such as locomotive and boiler tubes, which are required to withstand high temperatures, since mechanically hardened arsenical copper is not softened at so low an annealing temperature as pure electrolytic copper, which has undergone the same treatment.

Arsenic appears to improve the hot-working properties of copper vitiated by traces of bismuth.

Bismuth.—Bismuth is the most injurious impurity in copper, as very small quantities render the copper unworkable. According to Hampe, copper containing as little as 0.02 per cent. of bismuth is red-short, and 0.05 per cent., cold-short. With 0.1 per cent. the copper crumbles under the hammer at a red heat. The presence of certain proportions of arsenic and antimony somewhat counteracts the tendency of bismuth to produce cold-shortness.

Lead.—Lead can be melted with copper in all proportions, but the greater part of it can be liquated out of the alloy by a gentle heat. Lead is to be found in all ordinary commercial copper, but it is not desirable in any proportion over 0.10 per cent., and the lower the proportion under 0.10 per cent. the better. According to Hampe's experiments, 0.15 per cent. of lead does not affect the malleability of copper in any way; with 0.3 per cent. of lead it becomes slightly red-short, and with 0.4 per cent. slightly cold-short. With 1 per cent. it is unworkable. The lead reduces the strength, ductility and toughness of copper. The solvent action of copper for lead is very small. The addition of lead to copper has the effect of lowering the affinity of copper for reducing gases.

Iron.—Iron forms no true alloy with copper; small admixtures of iron such as are contained in many varieties of copper have no injurious

[1] Min. Ind., Vol. XVIII, 1909.

effects upon it. It occurs in refined copper in the merest traces, which are quite harmless. When all the sulphur has gone from a charge of copper, in refining, a sample taken from the furnace shows an unblistered surface, and is said to be "set-copper." At this point all the iron has been eliminated except the merest trace.

Iron acts as a deoxidizer when added to copper. Copper containing only 1 per cent. iron is rendered feebly magnetic, will forge well at a red heat, is quite malleable, tough and strong, even in the presence of arsenic. It lacks the fluidity of pure copper when poured at the same temperature.

Nickel.—Nickel alloys with copper in all proportions. Traces of nickel in copper are beneficial, imparting strength and toughness. Nickel must be kept low if arsenic is present, 0.10 per cent. being quite sufficient to harden arsenical copper which has to withstand severe working. Below 0.05 per cent., even in the presence of arsenic, its effect upon the physical properties, excepting electrical conductivity, may be considered insignificant.

Cobalt.—Little is known about the influence of this metal on copper. According to F. Johnson, it toughens and strengthens copper when present up to at least 1 per cent. without impairing its hot-working qualities. Probably it acts very similar to nickel, conferring greater durability at high temperatures, while toughening, hardening, and strengthening the copper in the cold. Cobalt, in the low percentages in which it is found in copper, is, if anything, beneficial, and, moreover, it does not disagree with arsenic to so great an extent as nickel does.

Tin.—Tin hardens copper, more than any other element. It occurs very rarely in commercial copper being readily eliminated during the process of reducing the copper. Low percentages of tin improve the tensile strength, ductility and resistance to corrosion, and maintain these improvements at high temperatures, but the natural softness of copper and its red color are both materially removed. Its malleability is also decreased.

Tellurium.—A few thousandths of 1 per cent. of tellurium renders copper appreciably red-short; but very little is known of the effect of tellurium in commercial copper.

Sulphur rarely occurs in more than harmless traces in commercial copper, yet it may occur to the extent of 0.03 per cent. (SO_2) in electrolytic copper having a conductivity of 102.2 per cent. It derives its origin from the incomplete removal of sulphur from the sulphate liquor in which the copper cathodes were deposited, and from the sulphurous gases from the fuel of the reverberatory refining furnace where it is partially dissolved by the molten metal, as they pass over it on their way to the flue. In the first case the sulphate would probably be reduced to sulphide by the reducing action of poling, and in the second case, sulphur dioxide would be absorbed and retained as such. Cuprous sulphide is a

highly undesirable constituent of copper, and its presence in any alloy would be detrimental. Hampe finds that copper with 0.25 per cent. sulphur is still moderately malleable, but with 0.5 per cent. it becomes very cold-short, although not red-short.

Carbon is not at all absorbed by copper.

Pure copper or copper of more than usual purity, assaying, say, 99.8 per cent., is inferior to impure copper in mechanical properties, durability, and resistance to corrosion.

Copper, when cast in moulds, has the property of rising and becoming porous. Sound castings can only be obtained by means of special precautions, such as pouring at the lowest possible temperature, or pouring in an atmosphere of carbon dioxide.

Cupric Carbonate.—The normal carbonate has not been obtained. The two most important basic carbonates are:

(1) $CuCO_3,Cu(OH)_2$, which occurs native as malachite.
(2) $2CuCO_3,Cu(OH)_2$, which occurs native as azurite.

The first is obtained when sodium carbonate is added to a solution of copper sulphate. When these carbonates are slowly heated to 220° C. the carbonate is slowly converted into black cupric oxide.

The carbonates of copper are readily soluble in dilute sulphuric, hydrochloric, sulphurous and nitric acids. They are also readily soluble in ammonia and ammonia salts. They are partially soluble in sodium carbonate and in solutions of potassium cyanide.

Cupric Nitrate, $Cu(NO_3),3H_2O$.—Cupric nitrate may be obtained by the action of nitric acid upon cupric oxide, hydroxide, carbonate, or the metal itself. Copper is soluble in nitric acid, in all of its mineralogical combinations. Sulphides are decomposed, as solution takes place.

Cupric nitrate is very easily soluble in water.

Cupric Oxide, CuO (Black Oxide of Copper).—Cupric oxide occurs in nature as the rather rare mineral, *tenorite*. It may be prepared artificially by continued ignition of copper in contact with air; by exposing cupric sulphate to an intense red heat, or the carbonate, nitrate, or hydroxide to a moderate heat.

When caustic potash or soda is added by drops to a boiling solution of cupric salts till the acid is saturated the whole of the copper is precipitated as anhydrous black oxide, which may be freed from potash or soda by boiling with water.

Cupric oxide is a black powder, which rapidly absorbs moisture from the air. When heated it first cakes together and finally fuses, giving up part of its oxygen, and leaving a residue consisting of $CuO,2Cu_2O$. When heated with charcoal, or in a stream of carbon monoxide, marsh gas or hydrogen, it is reduced to the metallic state.

When the cupric oxide is gently heated with metallic copper, it is converted into cuprous oxide.

A mixture of cupric oxide with excess of sulphur is resolved at a red heat into cuprous sulphide, sulphur dioxide and a trace of cupric sulphate. If on the contrary, the cupric oxide is in excess, cuprous oxide and cupric sulphate are produced, and with only a trace of sulphur dioxide, excepting that when the heat is raised to the point at which the cupric sulphate is decomposed.

Cupric oxide has a strong affinity for acids, dissolving in them easily. It is soluble in sulphurous acid. It is insoluble in ammonia, but dissolves on the addition of a few drops of acid or ammonium carbonate. It is insoluble in dilute, but soluble in warm concentrated caustic soda or potash. Ferrous chloride converts cupric oxide into cuprous and cupric chlorides, with the formation of ferric oxide. Ferric chloride converts cupric oxide into cupric chloride, with the formation of ferric oxide.

Cupric oxide is reduced to cuprous oxide at 1050° C.

Cuprous Oxide, Cu_2O (Red Oxide of Copper).—Cuprous oxide occurs native as cuprite, the red oxide of copper. It is formed when finely divided copper is gently heated in a current of air or when a mixture of cuprous chloride and sodium carbonate is gently heated in a covered crucible.

Cuprous oxide is reduced to the metallic stage by gentle ignition with charcoal or hydrogen.

Cuprous oxide is insoluble in water; it is converted into cuprous chloride by hydrochloric acid. Nitric acid converts it into cupric nitrate with the evolution of oxide of nitrogen. When acted upon by dilute sulphuric acid, it is partly reduced to metallic copper and partly oxidized into copper sulphate. When heated with strong acid it is entirely oxidized to sulphate.

When copper is oxidized with a considerable quantity of oxygen at a high temperature, it forms *cupric oxide* (CuO). If the ignition be carried further, *cuprous oxide*, Cu_2O, may be formed from the CuO. The cuprous oxide is not as readily soluble as the cupric oxide, and it may be partly for this reason that copper sulphides roasted at a high temperature do not give a good extraction of the contained copper.

Cuprous oxide fuses at a red heat.

When heated with acids coprous oxide forms a solution of a cupric salt and metallic copper; for example,

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

However, strong hydrochloric acid does not deposit metallic copper on dissolving cuprous oxide, which is due to the fact that the cuprous chloride formed is soluble in strong hydrochloric acid.

Cupric Sulphate, $CuSO_4,5H_2O$.—Copper sulphate may be formed

by applying dilute sulphuric acid to copper oxide, when the sulphate crystallizes out on cooling; by heating metallic copper with concentrated sulphuric acid, whereupon sulphur dioxide is evolved, and anhydrous cupric sulphate is precipitated as a white powder, mixed with a brown mass of cuprous and cupric sulphides; on digesting this mass with hot water, the cupric sulphate dissolves, and may be crystallized out of the solution.

On roasting, the sulphide ores of copper are converted into cupric oxide and cupric sulphate. When water is applied to the roasted ore, the copper sulphate is dissolved; by evaporation of the water, the copper sulphate crystallizes out of the solution.

At 100° C. copper sulphate loses 4 molecules of water, and at 200° it loses all its water. At a bright red heat it decomposes into copper oxide and sulphuric acid. When heated with carbon at a dark red heat the copper is separated, with the formation of carbonic acid and sulphur dioxide.

From solutions of copper sulphate, the copper is precipitated by means of iron, aluminum, and zinc, as metallic copper; with hydrogen sulphide or the sulphide of the alkali metals, it is precipitated as the cupric sulphide (CuS). By electrolysis, copper is deposited from copper sulphate solutions at the cathode and acid liberated at the anode. If at the anode, ferrous sulphate is present in the solution, it is converted into ferric sulphate.

The crystallized copper sulphate dissolves in 3 1/2 parts of cold water, and in much smaller quantities of boiling water.

SOLUBILITY OF COPPER SULPHATE

In 100 parts of water, at the following temperatures

Temperature		Parts $CuSO_4$	Per cent. copper
C.	F.		
0	32.0	14.15	4.00
10	50.0	17.50	4.95
20	68.0	20.53	5.81
30	86.0	24.34	6.88
40	104.0	28.50	8.07
50	122.0	33.31	9.43
60	140.0	39.01	11.04
70	158.0	45.74	12.93
80	176.0	54.53	14.33
90	194.0	64.35	18.23
100	212.0	75.22	21.28

All of the chlorides have the faculty of converting copper sulphate, in solution, into the chloride. Hydrochloric acid dissolves copper sulphate

with considerable reduction of temperature, forming a green liquid, which when evaporated forms crystals of cupric chloride.

When excess of ammonia is added to a solution of copper sulphate, a deep blue solution is formed having the composition $CuSO_4,H_2O,4NH_3$.

Cupric and ferrous sulphates cannot be entirely separated by crystallization, as a solution of these salts deposits a double sulphate of the two metals. If, however, the amount of iron present is comparatively small, the first crop of crystals obtained is moderately pure copper sulphate.

Cupric Chloride, $CuCl_2$.—Cupric chloride may be obtained in the anhydrous condition by the combustion of copper in an atmosphere of chlorine gas; copper filings or copper foil introduced into dry chlorine takes fire spontaneously, and burns with a greenish light, producing a mixture of cupric and cuprous chlorides, and if the chlorine is in excess the cuprous chloride is slowly converted into the cupric chloride. It is also produced when compounds of copper are roasted with salt or other chlorides.

In the wet way it is formed when copper is dissolved in nitro-hydrochloric acid (aqua regia), or when cupric oxide, carbonate, or hydroxide are dissolved in hydrochloric acid. Cupric chloride is readily soluble in water, forming a deep green solution, which on being largely diluted, turns blue. The salt crystallizes in green rhombic prisms, with $2H_2O$, giving the composition of the crystals as $CuCl_2,2H_2O$. When heated to 200° C. it loses its water of crystallization, and at a dull red heat is converted into cuprous chloride, with evolution of chlorine.

With copper oxides cupric chloride combines in various proportions to form oxychlorides. From solutions of cupric chloride metallic copper is precipitated by iron, aluminum, and zinc. With hydrogen sulphide and the sulphides of the alkali metals and earths the copper is precipitated as cupric sulphide, (CuS). Calcium hydroxide, or lime, precipitates copper as the hydroxide, which on heating, is converted into the oxide. By passing sulphur dioxide into a solution of cupric chloride, the copper is precipitated as the cuprous chloride.

By electrolysis, copper is deposited from cupric chloride solutions at the cathode, while chlorine is liberated at the anode.

SOLUBILITY OF CUPRIC CHLORIDE IN WATER

In 100 parts of water, at the following temperatures

Temperature		Parts $CuCl_2$	Per cent. copper
C.	F.		
0	32	70.6	33.6 per cent.
17	62	76.2	36.3 per cent.

100 parts of water, saturated with $CuCl_2$, contains, at the following temperatures:

Temperature		Parts $CuCl_2$	Per cent. copper
C.	F.		
0	32	41.4	19.7 per cent.
17.0	62	43.1	20.4 per cent.
31.5	88	44.6	21.2 per cent.

100 grm. of water dissolve 121.4 grm. of $CuCl_2+2H_2O$, at 16.1° C.

Cupric chloride is not decomposed by cold sulphuric acid.

It is soluble in solutions of ammonium chloride, and very soluble in concentrated solutions of common salt. It is less soluble in concentrated solutions of hydrochloric acid than in dilute solutions.

With ammonia cupric chloride forms a deep blue solution having the composition $CuCl_2,4NH_3,H_2O$.

Cuprous Chloride, Cu_2Cl_2.—Cuprous chloride may be obtained by dissolving cuprous oxide in hydrochloric acid. It is more readily prepared by boiling a solution of cupric chloride in hydrochloric acid, with copper foil or copper turnings. The nascent hydrogen, liberated by the action of hydrochloric acid upon the copper, reduces the cupric chloride to the cuprous chloride. The liquid is then poured into water, which causes the precipitation of the cuprous chloride as a white crystalline powder. A mixture of zinc dust and copper oxide added to strong hydrochloric acid, also yields cuprous chloride, the nascent hydrogen in this case being derived from the zinc, and this causes the reduction of cupric chloride formed by the action of the acid upon the cupric oxide.

Cuprous chloride may be formed by heating the cupric chloride to a dull red heat.

Cuprous chloride melts somewhat below a dull red heat, and when slowly cooled, solidifies in a translucent yellow mass. In closed vessels it does not volatilize, even when strongly heated, but if heated in the air it goes off in white vapor. When exposed to the air in a dry state it slowly absorbs moisture and turns green; in the moist state it is quickly turned into a green mass, of oxychloride of copper, $CuCl_2,3CuO,4H_2O$. This compound occurs native as the mineral Atacamite.

Cupric chloride, $CuCl_2$, when ignited gives cuprous chloride, and therefore cuprous chloride is always formed when copper enters into reaction with chlorine at a high temperature. The green solution of cupric chloride is decolorized by metallic copper, cuprous chloride being formed; but this reaction is only accomplished with ease when the solu-

tion is very concentrated and in the presence of an excess of hydrochloric acid to dissolve the cuprous chloride. The addition of water precipitates cuprous chloride.

Many reducing agents which are capable of taking up half the oxygen from cupric oxide are able, in the presence of hydrochloric acid, to form cuprous chloride; sulphur dioxide, SO_2, acts in this manner. The usual method of preparing cuprous chloride consists in passing sulphur dioxide into a strong solution of cupric chloride.

Cuprous chloride forms colorless cubic crystals which are insoluble in water. Under the action of oxidizing agents, it passes into cupric salts and it absorbs oxygen from the moist air, forming cupric oxychloride.

From solutions of cuprous chloride, metallic copper is precipitated by iron, aluminum, and zinc. Hydrogen sulphide and the sulphides of the alkali metals and earths, precipitate the copper as cupric sulphide, CuS.

By electrolysis, copper is deposited at the cathode, while chlorine is liberated at the anode. If univalent salts are present in the anode solution, these will be converted into bivalent salts by the action of the liberated chlorine.

Milk of lime, added to a hot solution of cuprous chloride, precipitates the copper as cuprous oxide.

Cuprous chloride is insoluble in water, but dissolves in hydrochloric acid, ammonia, and alkaline chlorides.

SOLUBILITY OF CUPROUS CHLORIDE IN SOLUTIONS OF SODIUM CHLORIDE

Saturated sodium chloride solution dissolves at

Degrees C.	Degrees F.	Cuprous chloride, Cu_2Cl_2	Metallic Cu
90	194	16.9 per cent.	10.76 per cent.
40	104	11.9 per cent.	7.65 per cent.
11	51.8	8.9 per cent.	5.73 per cent.
		15 per cent. NaCl-Aq. dissolves at	
90	194	10.3 per cent.	6.62 per cent.
40	104	6.0 per cent.	3.86 per cent.
14	57.2	3.6 per cent.	2.31 per cent.

		5 per cent. NaCl-Aq. dissolves at	
90	194	2.6 per cent.	1.67 per cent.
40	104	1.1 per cent.	0.71 per cent.

Cuprous chloride, when melted, conducts the electric current very well, copper separating out as fine leaves. The melt cannot be heated to the melting point of copper and the copper obtained liquid, because the cuprous chloride vaporizes too easily.

Cupric Silicate, $CuSiO_3+2H_2O$.—Silicate of copper occurs native as chrysocolla, $CuSiO_3+2H_2O$, and dioptase, CuH_2SiO_4. Chrysocolla is soluble in dilute hydrochloric acid, leaving a residue of silica. Dioptase is soluble in nitric and hydrochloric acids, or ammonia, with separation of gelatinous silica. It is not attacked by caustic alkalies.

Cuprous Sulphide, Cu_2S.—There are two sulphides of copper, corresponding to the two oxides; the cuprous sulphide, Cu_2S, and the cupric sulphide, CuS.

The cuprous sulphide, when heated at a comparatively low temperature, loses one-half of its sulphur and is converted into the cupric sulphide.

Cuprous sulphide occurs in nature as copper glance, or chalcocite. It is produced artificially when copper burns in sulphur vapor, or when an excess of copper filings is heated with sulphur.

It is not decomposed out of contact with the air; but if air has access to it, combustion takes place, and sulphur trioxide and cupric oxide are produced. When heated to redness in a current of aqueous vapor, it is but slightly decomposed, but at a white heat, it yields large quantities of hydrogen and hydrogen sulphide together with sublimed sulphur, and the copper is completely reduced to the metallic state. It is not altered by ignition in a stream of hydrogen.

It is not decomposed by chlorine gas at ordinary temperatures; very slowly when heated. It dissolves with difficulty in strong boiling hydrochloric acid. In heated nitric acid it dissolves with separation of sulphur, whereas cold nitric acid dissolves one-half the copper, and leaves the cupric sulphide. Cuprous sulphide, ignited with cuprous oxide, is easily converted into sulphur dioxide and copper or cuprous oxide. It is not dissolved by sulphuric acid. It is slowly acted upon by solutions of ferric chloride and of ferric sulphate. Cuprous sulphide melts at 1127° C.

Cupric Sulphide, CuS.—Cupric sulphide is met with in nature as the mineral covelite (blue copper). It is obtained artificially when either copper or cuprous sulphide is heated with sulphur to a temperature not beyond 114° C.; so obtained, the compound is blue. As a black precip-

itate, it is formed when hydrogen sulphide is passed into solutions of cupric salts.

Treated with hot nitric acid the copper is oxidized, part of the copper is converted into sulphate and the rest separated, so that the resulting solution contains both nitrate and sulphate of copper. Hot concentrated hydrochloric acid slowly converts it into cupric chloride, with evolution of hydrogen sulphide and separation of sulphur. Cupric sulphide decomposes silver salts, the copper dissolving and the sulphide of silver being precipitated. It is insoluble in dilute sulphuric acid, caustic alkalies, and fixed alkaline sulphides. It is slightly soluble in ammonium sulphide.

Cupric Hydroxide, $Cu(OH)_2$.—Cupric hydroxide is a pale blue precipitate produced when sodium or potassium hydroxide is added in excess to a solution of a copper salt. The compound, when washed, may be dried at 100° C., without parting with water; but if the liquid in which it is precipitated be boiled, the compound blackens, and is converted into a hydrate having the composition $Cu(OH)_2$, $2CuO$. Cupric hydroxide dissolves in ammonia, forming a deep blue liquid. It is very soluble in acids. It is changed, by standing, to the black compound, $Cu_3O_2(OH)_2$ and by boiling to cupric oxide, CuO.

Ammonium carbonate, like ammonium hydroxide, precipitates the cupric hydroxide and redissolves it to a blue solution. Carbonates of the fixed alkali metals, as potassium and sodium carbonate, precipitate the greenish-blue carbonate, $Cu_2(OH)_2CO_3$, which is converted by boiling to the black, basic hydroxide, and finally to the black oxide.

From the blue ammoniacal solutions a concentrated solution of a fixed alkali precipitates the blue hydroxide, changed on boiling to the black oxide, CuO.

Cupric hydroxide is soluble in a solution of cane sugar in the presence of an alkali or alkaline earth. It is somewhat soluble in the caustic alkalies, and very soluble in ammonia.

Copper Cyanides.—Potassium cyanide forms, with copper, the yellowish-green cupric cyanide, $Cu(CN)_2$, soluble in excess, with the formation of the double cyanide, $2KCN, Cu(CN)_2$, unstable, changing in whole or in part to cuprous cyanide. The potassium cyanide also dissolves cupric oxide, hydroxide, carbonate, sulphide, etc., changing rapidly to cuprous cyanide in solution in the alkali cyanide.

Potassium ferrocyanide precipitates cupric ferrocyanide, reddish-brown, insoluble in acids, decomposed by alkalies; a very delicate test for copper (1 to 200,000); forming in highly dilute solutions a reddish coloration.

Solubility of Sulphur Dioxide, SO_2.—Sulphur dioxide is largely used in the hydrometallurigcal methods of extracting copper from its ores. Lunge gives the percentage of a saturated solution of sulphur dioxide in water, as follows:

Temperature, degrees		Percentage
C.	F.	SO_2
20	68	8.6 per cent.
30	86	7.4 per cent.
40	104	6.1 per cent.
50	122	4.9 per cent.
60	140	3.7 per cent.
70	158	2.6 per cent.
80	176	1.7 per cent.
90	194	0.9 per cent.
100	212	0.1 per cent.

The normal quantity of SO_2 in burner-gas from brimstone burners is 11.23 per cent. by volume and 8.75 per cent. from burning pyrities.

Sulphur dioxide from roasting furnaces is much more dilute; muffle furnaces give a very much more concentrated gas than reverberatories.

SOLUBILITY OF SO_2 IN WATER (Watts Dictionary)
Absorbed by 1 grm. of water at 760 mm.

Temperature, degrees C.	Grm. SO_2	C.c. SO_2
8	0.168	58.7
12	0.142	49.9
16	0.121	42.2
20	0.104	36.4
24	0.092	32.3
28	0.083	28.9
32	0.073	25.7
36	0.065	22.8
40	0.058	20.4
44	0.053	18.4
48	0.047	16.4
50	0.045	15.4

One liter of SO_2 weighs 2.86336 grm. 1 cu. ft. weighs 0.1787 lb. With water, sulphur dioxide does not form sulphurous acid proper, H_2SO_3. The sulphur dioxide dissolves pretty freely in water, and this solution behaves in every way as if it contained the real acid, H_2SO_3.

The solution of SO_2 by volume in water at various temperatures is as follows:

1 volume of water at 0° C.— 32° F. dissolves 79.789 volumes SO_2
1 volume of water at 20° C.— 68° F. dissolves 39.374 volumes SO_2
1 volume of water at 40° C.—104° F. dissolves 18.766 volumes SO_2

CHAPTER IX

HYDROMETALLURGICAL PROCESSES

Classification and General Consideration.—Hydrometallurgical processes for the extraction of copper from its ores or matte may be considered as:

Purely Chemical and
Electrolytic.

In the purely chemical processes the copper is dissolved and precipitated by chemical reagents; in the electrolytic processes, the copper is dissolved chemically but the precipitation is effected electrolytically, accompanied, usually, by regeneration of the solvent.

Chemical Processes.—These may be classified as follows, based mostly on the solvent employed:

Alkali processes,
Sulphite processes,
Sulphate processes,
Chloride processes.

Nitric acid, by means of which the copper would be dissolved as the nitrate or sulphate, has been frequently suggested as a solvent of copper from its ores. The fixation of atmospheric nitrogen by electricity, offers a cheap way of producing nitric acid at the mines. There are, however, inherent difficulties to the use of nitric acid which makes its application questionable. Nitric acid is the best known solvent of copper, but it is also an excellent solvent of all the impurities in the ore, so that insurmountable difficulties may be expected, both in the solution of the copper and in its precipitation, if regeneration of the solvent is desired.

The applicability of any solvent process to the extraction of copper, depends fundamentally on the character of the ore. All acids, likely to be used in a solvent process, react more or less with other elements; when so consumed the acids are unavailable for useful work, and frequently bring into solution ingredients which are positively harmful The elements most detrimental to acid processes are:

Calcium,
Magnesium,
Aluminum,
Zinc,
Manganese.

To these may be added iron, arsenic, antimony, bismuth; but these elements need not necessarily be fatal to an acid process, no matter in what proportion they occur in the ore.

If lime, magnesia, zinc or manganese occur in the ore in large quantities, acid processes are not applicable. What the limit is, can only be determined by direct experiment. Chemical analysis of the ore, while instructive, cannot be relied upon to determine the applicability of an acid process. Lime, for example, is only detrimental in certain combinations, as the oxide or carbonate. In many ores where sulphuric acid has been a factor in the deposition or in the oxidation of the vein matter, much of the calcium will be found as sulphate, which is not particularly injurious either in a sulphate, sulphite or chloride process. All of this calcium, however, would usually be estimated as lime (CaO), although it occurs as sulphate ($CaSO_4$). Magnesia is highly injurious as oxide and carbonate, but magnesia is not as widely distributed as lime, in injurious amounts.

Alumina is widely distributed, but its presence, while undesirable, is not necessarily particularly injurious. Much depends on its mineralogical combinations. In Cripple Creek, sulphuric acid has been used for many years in connection with the chlorination of those ores, which contain from 15 to 20 per cent. alumina. Zinc, especially as the oxide, is injurious, because it is readily soluble in acids, and as yet no practicable method has been found for its economic precipitation. Electrolytic precipitation offers a plausible way of recovering the zinc, and is in practical use in several plants, but its general adoption is by no means assured.

Many oxidized ores are improved by roasting. All sulphide ores, with the possible exception of certain chalcocite deposits, should be roasted before chemical treatment, no matter what the nature of the chemical treatment may be.

The treatment of raw sulphide ores has never met with much encouragement, and the cause for this is reasonable enough. The highly oxidized ore is in the best possible condition for the application of any solvent, and it is difficult to conceive of any oxidizing process, or substitution for an oxidizing process, cheaper and more satisfactory than roasting. It is true that low grade ores have been treated in Spain and Portugal by natural weathering, and for a while with ferric chloride or ferric sulphate, but the use of ferric chloride has long since been abandoned, and the slow process of weathering, in which years are required to get an adequate extraction, is perhaps nowhere else applicable.

It may be considered, therefore, in hydrometallurgical processes, that the application of the solvent is to the oxidized ores.

Many of the metal compounds as found either in raw or roasted ore, have the faculty of reducing the ferric to the ferrous salts, the respective

metals being thereby brought into solution. This is notably the case with ferric sulphate, $Fe_2(SO_4)_3$, and ferric chloride, $FeCl_3$. Both of these substances have been used, and have been extensively experimented with in the reduction of copper ores, by hydrometallurgical methods. The leaching method at present used at Rio Tinto, Spain, is based mostly on the solvent action of ferric sulphate, and the Doetsch process, formerly used there extensively, was based on the solvent action of ferric chloride.

CHAPTER X

CHEMICAL PROCESSES

ALKALI PROCESSES

The alkali processes have not met with much encouragement in the hydrometallurgical extraction of copper from its ores. This is due largely to the slow and low solubility of copper in a solution of the alkalies. Ammonia and ammonium compounds are about the only alkaline solvents which have been tried on a commercial scale. The oxides and carbonates of copper are quite readily soluble in ammonia but the solution should take place in tight receptacles as the volatility of the gas in aqueous solution is quite perceptible. If ammonium carbonate is used on calcareous ores there should be no sulphates present, because they would be decomposed into ammonium sulphate and calcium carbonate.

After the copper is dissolved the ammoniacal copper solution is boiled, and the black oxide of copper precipitated. The ammonia vapor boiled off may be condensed in towers and used on another charge of ore. The recovery of the ammonia from the salts formed in the boiled-out solution may be accomplished by means of lime and steam.

According to Schnabel[1] experiments hitherto tried in using ammonia or ammonium carbonate have failed because ammonia-tight vessels were not employed, and because the precipitation of the copper, for which iron cannot be employed, was performed by means of hydrogen sulphide, calcium sulphide, or barium sulphide. By the use of iron vessels, however, loss of ammonia may be avoided, but such apparatus has proved complicated and expensive to operate. The oxides of zinc, nickel, cobalt, etc., are also soluble in ammonia or ammonium carbonate.

Sodium carbonate has been suggested as a solvent of copper from oxide and carbonate ores, but the solubility of copper in sodium carbonate is so unsatisfactory that experiments along these lines have not been encouraging. Copper is also slightly soluble in concentrated solutions of the caustic alkalies. Schneider[2] purposes increasing this solubility by the addition of glycerin.

The Mosher-Ludlow Ammonia-cyanide Process.[3]—This process depends upon the principle that ammonia, NH_3, at the ordinary temperature forms soluble, stable compounds with the oxides, hydroxides or carbonates of copper, zinc, nickel, or cobalt, such as $Cu(NH_3)_2$.

[1] Handbook of Metallurgy, Vol. I, p. 204.

[2] U. S. patent 932, 643, Aug. 31, 1909.

[3] *Electrochemical and Metallurgical Industry*, March 1908.

These ammonia metal compounds are readily dissolved by water containing a small excess of ammonia over that required to form the soluble compound. This is the leaching step of the process.

The step of precipitation depends on the fact that those soluble ammonia-metal compounds break up with great ease at the boiling point of water into the oxide or hydrate of the metal, which almost instantly settles as a heavy precipitate, while the ammonia, originally combined, is set free to be reabsorbed in cold water or boiled-out solution for use over and over again.

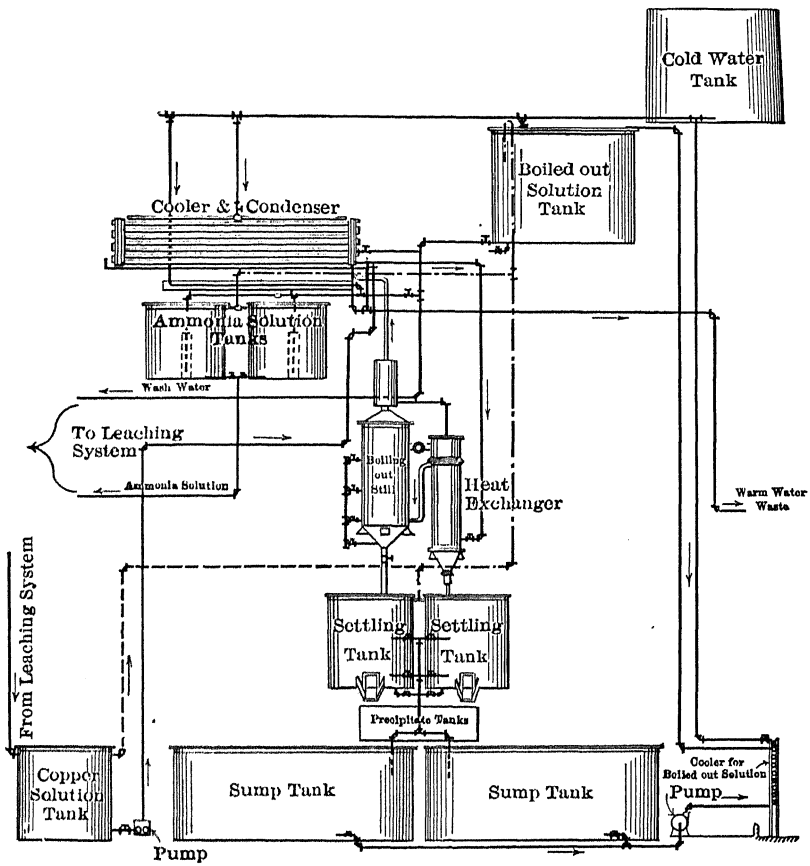


FIG. 44.—Moser-Ludlow ammonia-cyanide process. Diagrammatic sketch.

Where the percentage of copper is large the aim is to first extract as much of the copper as possible by plain ammonia, and to leave the gold and silver values to be subsequently extracted with a weaker ammonia solution containing fractional percentages of potassium cyanide. But instead of working it in this way it may be preferable in many instances to add the cyanide at once to the ammonia and to simultaneously ex-

tract all the values, including copper, gold, and silver, with an ammoniacal solution containing one to several pounds of cyanide per ton. The object aimed at is to reduce the comsumption of cyanide to a minimum in the presence of copper, thereby permitting the minute amounts of potassium cyanide added to the ammonia solution to simultaneously extract the gold and silver values.

To recover the metallic values from the ammonia-cyanide copper-gold-silver bearing solution, it is passed through a continuous boiling-out still, to precipitate the copper as CuO. The boiled-out solution holding the gold and silver values is agitated with the least amount of zinc dust, or passed through zinc boxes to recover such gold and silver as the boiled-out solution may contain.

For treating the ore containing considerable percentages of ammonia-soluble metals, the chlorination barrel, without lead lining is recommended. In the treatment of slimes, agitation in a closed conical tank, with subsequent filtering with any of the well-known filters.

On account of the powerful oxidizing action of a solution of cupric oxide (CuO) in ammonia, unoxidized silver minerals may be attacked and finally dissolved in the raw state, obtaining in this manner a percentage of extraction out of this character of mill product entirely impossible by ordinary cyanide methods.

It is of the greatest importance to have a thoroughly ammonia-tight equipment, especially in the second half of the process, which comprises the boiling out of the ammonia solution. This apparatus is designed so that the boiling out is carried on continuously, and it may in some way be compared to the artificial ice and cold storage apparatus in which the ammonia water is boiled in a still, the ammonia gas distilled off, liquefied under pressure by powerful pumps, then permitted to expand, by which the cooling effect is produced, and finally reabsorbed in cold water to commence the same cycle of action over and over again.

In the Mosher-Ludlow continuous boiling-out apparatus the incoming cold ammonia-copper solution is brought in contact with the heat of the ammonia-steam vapor in the cooler and condenser and in the heat exchanger on its way to the boiling-out still, with the overflowing boiled-out solution. In this way an important part of the heat applied to boil out the ammonia is passed to the incoming solution, thus saving steam and fuel.

The ammonia-copper solution is taken from the copper-solution tank and pumped through the inner coil of a double-pipe counter-current cooler; thence it passes to the heat exchanger, thence to the boiling-out still, thence into the exchanger, where part of its heat is passed to the incoming solution; thence to the settling tanks, where the precipitate, which is almost pure copper oxide, is allowed to settle, the liquid being drawn off into the sump tanks. From the sump tanks the boiled-out

solution is pumped through a cooler up to the boiled-out solution tank. From there it is used as needed to make fresh ammonia solution, and as wash water.

The ammonia and steam vapor from the boiling-out still passes up to the cooler and condenser into the annular spaces between the two pipes, parting with a fraction of its heat to the incoming ammonia-copper solution in the inner pipe. From the cooler and condenser the ammonia water flows into the ammonia solution tanks where it is diluted and is ready to be sent to the leaching system. A supply of cold water is kept flowing over the outside of the cooler and condenser and the boiled-out solution cooler. The precipitate is removed from the settling tank from time to time, as required.

It is estimated that the heat required in boiling out 2 per cent. ammonia-copper solution on a 100-ton (24-hour) basis, and precipitating the copper as black oxide =79.9 per cent. copper, is 51,083,000 b. t. u. of which, however, according to experience, 60 per cent. is saved by the heat exchanger, so that the net heat required amounts to 34,333,000 b. t. u. In practice this required heat can be obtained from 1 1/2 to 2 tons of good coal, and with a boiler of from 35 to 40 h. p.

SULPHITE PROCESSES

A solution of sulphur dioxide in water may be regarded as sulphurous acid, (H_2SO_3). Copper oxide and carbonate are soluble in sulphurous acid, the sulphide is not.

Various methods have been suggested for the practical use of sulphurous acid as a solvent of copper from its ores. All of these refer more directly to the precipitation of the copper from the sulphurous acid solution, rather than the solution of the copper from the ore. Copper sulphite is not soluble in water, but is readily soluble in excess of sulphurous acid. Copper sulphite is an unstable salt, which is slowly changed into a mixture of cupro-cupric sulphite and cupric sulphate, as shown by the following reactions:

(1) $3CuO + 3SO_2 = 3CuSO_3$.

(2) $3CuSO_3 + CuO = Cu_2SO_3,CuSO_3 + CuSO_4$.

The cupro-cupric sulphite is only very slightly soluble in water, but is quite soluble in sulphurous acid or in a solution of copper sulphate.

Neill Process.—This process consists, first in subjecting the ore to the action of sulphurous acid to dissolve the copper, and second, in heating the solution to drive off the excess of sulphurous acid and precipitate the copper as sulphite.

If the ore to be treated is a sulphide it has to be roasted; if the ore is an oxide or carbonate it may be treated without roasting. The sulphur dioxide used in the process may be obtained from burning sulphur or

from roasting sulphide ores, which if they are copper ores, may be subsequently treated in the oxidized condition with the sulphur dioxide obtained from the roasting.

There is less sulphur required to extract the copper as sulphite than as sulphate. It takes 98 lb. of sulphuric acid to dissolve 63 lb. of copper, as sulphate, while it only takes 32 lb. of sulphur, in the form of sulphurous acid, to dissolve the same amount of copper—63 lb. The sulphurous acid may be applied either as a gas or in solution, or a combination of both.

In practice, the ore is crushed to a suitable degree of fineness and charged into agitation tanks, and agitating the ore in contact with the sulphurous acid; or the agitation may be effected in tanks having a conical bottom, by forcing sulphurous acid mixed with more or less air, through the pulp. In this way the sulphurous acid is applied to the ore while air does the agitating. The tanks, or agitators, in which the ore is treated may be closed at the top, so that the excess of gas issuing from the first tank may be passed through the second and so on until the sulphur dioxide is entirely consumed.

The clear solution, after being separated from the ore by either filtration or decantation, is heated to a temperature sufficient to drive out the excess of sulphurous acid, thereby precipitating the copper in the form of a bright-red and very heavy powder (cupro-cupric sulphite). The cupro-cupric sulphite settles at once to the bottom of the precipitating tank, and the supernatant liquor may be decanted or siphoned from it, or the sulphite may be recovered from the solution by filtration. The excess of sulphurous acid, driven out of the solution by heating, may be recovered for re-use. The cupro-cupric sulphite after it has been removed from the tanks, filtered and dried, contains about 50 per cent. metallic copper. This precipitate may be heated in an oxidizing atmosphere in a furnace and the cupric oxide produced, or it may be melted in a reducing atmosphere, producing cuprous sulphide, which may then be reduced to metallic copper by the ordinary converter process.

With ores suited to the process, the copper will pass into solution in from 1 to 4 hours. When the copper is dissolved by sulphurous acid, only very small amounts of other metals are dissolved, and the ultimate product is a very pure copper.

Should any copper exist in the solution as sulphate, due either to improper roasting, or of sulphur trioxide in the sulphurous acid, this sulphate of copper will not be precipitated by boiling the solution, but must be precipitated in some other way. This may be done either with iron or by electrolysis.

If a solution of cupro-cupric sulphite is heated at a high temperature (about 200° C.) and subjected to a pressure of about 25 lb., sulphur dioxide is liberated, and there is formed copper sulphate and metallic copper.

About one-half of the copper may in this way be precipitated in the metallic condition.

Neill Process at Coconino, Arizona[1] According to Jennings, the original method as carried out at Coconino, consisted in treating the ore, with sulphur dioxide, in a series of upright tanks 8 ft. in diameter and 18 ft. high. About 5 tons of ore were introduced into the tank half filled with water, and gas was forced, by means of a compressor, into this mixture of ore and water, the excess gas passing from the first tank to a similar one, also charged with ore and water, and thence to a third tank, where it was supposed the absorption would be complete. The gas was not all used up owing to the difficulty of absorbing sulphur dioxide in water when mixed with large volumes of air. When the ore in the lower tank was leached, an operation which usually took 10 hours' time, the solution and the leached ore together were dropped into a pressure tank and thence passed into a large filter press. The filter press was a constant source of trouble as it was impossible to find a material for the filters which would stand any length of time.

The solution from the filter press was heated by waste steam from the crushing plant and 60 per cent. of the copper precipitated as cupro-cupric sulphite.

Jennings gives the weak points of the Neill process as carried out at Coconino, as: 1. The attempt to saturate the water by simply blowing the gas through it; 2. the poor agitation obtained and the consequent length of time required to leach a comparatively small amount of ore; 3, the dilute solution obtained, 1 per cent. being the maximum amount of copper which can be held in solution by an excess of SO_2; 4. the ease with which the copper separates from these solutions, both in the leaching tanks, the pressure tank and the filter tanks, forming the cupro-cupric precipitate throughout the mass of leached ore, and which it was impossible to redissolve with sulphurous acid, and 5. the difficulty of treating the remaining 40 per cent. of the copper in solution as sulphate after the 60 per cent. has been precipitated. Scrap iron was not cheaply available.

It is evident that many of the weak points here enumerated by Jennings should not present much difficulty in a well designed plant. The effective absorption of gases in liquids, has long been satisfactorily accomplished in the chemical industry, by some means of subdivision; agitation is accomplished successfully on an enormous scale in the cyanide process, where it is necessary to bring air in contact with the ore and cyanide solution, to effect extraction. In experiments made by Jennings[2] on the same, or similar copper-bearing triassic sandstones of northern Arizona, he succeeded in getting an extraction of 95 per cent. of the copper, with sulphur dioxide, by leaching the ore 4 hours. The low copper content of the solutions was due to the small excess of sulphur

[1] E. P. Jennings, *E. and M. J.*, Jan. 18, 1908.

dioxide. In later experiments[1] Mr. Jennings succeeded in getting as high as 2 per cent. copper in the solutions.

It is evident that, so far as the operations at Coconino are concerned, it leaves the process where it was before the plant was erected. It demonstrated neither technical failure nor success.

Neill, the inventor of the process, in experiments carried out in Salt Lake City[2] succeeded in getting a complete extraction of Coconino ore, having 11 per cent. copper, in 6 hours. He readily obtained a solution carrying 2.5 per cent. copper, and so long as the solution remained cool no difficulty was experienced with the copper separating out in the sands, or in washing the sands.

An experimental plant, installed at the smelter of the Montana Ore Purchasing Company at Butte, by Neill, gave interesting results. The material was roasted to about 2 per cent. sulphur content. It was then placed in a wooden barrel 6 ft. in diameter and 12 ft. long, and SO_2 gas from the roasting furnace was blown through the hollow trunions and brought into more intimate contact with the pulp by means of wooden paddles arranged on the sides and periphery of the barrel. Two tons of roasted ore were charged with 5 tons of water, and after passing the dilute roasting gases through the barrel for 6 or 8 hours the copper was successfully extracted. The barrel was dumped into a settling tank, the solution drawn off by percolation, and the sands washed in the same way. This washing was difficult on account of the ferric oxide, which being flocculent, remained in suspension and formed a layer upon the top of the sands which it was difficult to percolate. The sands after this incomplete wash averaged 0.8 per cent. copper, but average samples taken from the tank and washed by agitation and decantation, gave final tails of 0.31 per cent. copper. The heads averaged 3.15 per cent., showing an extraction of 90 per cent. The solution was heated in a wooden tank by a steam coil, and the precipitates, which were slightly contaminated with alumina, on account of the poor filtration, amounted to 64 per cent. of the copper extracted. The remainder was precipitated upon iron in a splash tank and the final solution turned to waste carried only traces of copper.

The amount of iron consumed was exceedingly small and the reaction very quick, owing to the fact that the solution came from the steam tanks at nearly the boiling point.

There were 35 tons of material treated, and the figured cost of the operation compared favorably with anything being done at that time or now in the Butte district. The process was not adopted because at that time the silver content of the company's ore was high and could not be saved by this method, and the space necessary for the plant was not available.

[1] *E. and M. J.*, April 18, 1908.
[2] *E. and M. J.*, March 14, 1908.

Van Arsdale Process.[1]—The van Arsdale process consists in precipitating copper from cupric sulphate solutions and simultaneously producing sulphuric acid, by adding to solutions of cupric sulphate, sulphur dioxide and heating with or without pressure. The copper is thrown down in solid form which may be subsequently treated, while the regenerated acid is applied to the ore for the extraction of more copper.

The ore must contain the copper as oxide or carbonate. The original solution for leaching must contain cupric sulphate and should contain ferrous sulphate. The precipitation will proceed with cupric sulphate alone, resulting in the formation of a salt of copper and the formation of sulphuric acid; by the addition of ferrous sulphate the reaction proceeds better, and by the use of a proper proportion of ferrous sulphate there is obtained a precipitate of metallic copper. In practice the solutions will always contain more or less ferrous sulphate dissolved from the ores treated. Good results are obtained from a solution containing approximately 10 per cent. each of cupric sulphate and ferrous sulphate. To precipitate the copper, sulphur dioxide is applied to the solution to nearly saturation. The solution is then heated to nearly the boiling temperature, whereupon a reaction takes place, resulting in the precipitation of a part of the copper contained in the solution either as metallic copper or compounds of copper, or both, together with the formation of sulphuric acid. The amount of copper precipitated will vary with the composition of the solution and also with the pressure under which it is heated. When the solution is heated under pressure an increased precipitation of copper is obtained, amounting to about 50 per cent. of the copper originally present, and an amount of sulphuric acid regenerated amounting to about double that necessary to redissolve from ore the amount of copper precipitated. The process being cyclic, there is no particular harm in returning to the ore a solution containing a considerable amount of unprecipitated copper sulphate.

The chemical reactions involved in the process may be given as:

$$(1)\ 3CuSO_4+3SO_2+4H_2O=CuSO_3,Cu_2SO_3+4H_2SO_4.$$

$$(2)\ Cu_2SO_3,CuSO_3+4H_2SO_4=Cu+2CuSO_4+2H_2SO_4+2SO_2+2H_2O.$$

At atmospheric pressure and in the cold, a solution of cupric sulphate saturated with sulphur dioxide, after standing for some time, deposits a small amount of cupro-cupric sulphite. On heating such a solution to boiling and at the same time passing sulphur dioxide through it, a larger amount of copper is precipitated, resulting finally in a precipitate of metallic copper, according to equation No. 2. When the solution, however, is saturated with sulphur dioxide and placed in a closed vessel and heated under pressure, the yield of precipitated copper is increased to

[1] *E. and M. J.*, June, 1903; U. S. Patent, March 31, 1903, No. 723,949.

40 and 50 per cent. of the copper originally present, and free acid is formed according to the above equations.

The degree of heat and pressure required for the second operation are not high, it being only necessary to heat the saturated solution to nearly 100° C., the pressure produced being about 30 lb. to the square inch. A lead lined steel tank may be used for this purpose.

Jumau found[1] the following relations of temperature and proportion of copper precipitated from a copper sulphate solution saturated with sulphurous acid, having originally 25 grm. of copper sulphate per liter.

Temperatures	Copper precipitated
140° C.	47 per cent.
155° C.,	62 per cent.
167° C.,.	65 per cent.
190° C.,	79 per cent.

SULPHATE PROCESSES.

Ordinarily only oxidized ores such as the oxides and carbonates, can be treated so as to dissolve the copper as sulphate. Sulphides are not usually amenable, practically, to direct treatment. Roasting is desirable. After the ore is roasted the copper should be in the form of oxide and sulphate, although in improperly roasted ore sulphides may still be present. The roasted material is then treated the same as naturally occurring oxidized ores. The copper may be dissolved as sulphate either by

Sulphuric acid, or
Metal sulphates,

such as the ferric sulphate. The acid, however, is the solvent most universally employed.

If iron is used as the precipitant, as it usually is, the sulphuric acid process consists essentially of applying dilute sulphuric acid to the oxidized ores of copper, which reacts with the oxide of copper as follows:

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

The copper sulphate thus formed is filtered from the ore and precipitated with iron, thus:

$$CuSO_4 + Fe = Cu + FeSO_4,$$

the iron and the copper changing places. The copper is precipitated while the iron goes into solution as ferrous sulphate. From this reaction it will be seen that, theoretically, it takes 98 lb. of sulphuric acid to dissolve 63.6 lb. of copper, and 56 lb. of iron to precipitate 63.6 lb. of copper; 1.56 lb. of sulphuric acid to dissolve 1 lb. of copper and 0.88 lb. of iron to precipitate it. These equivalents are for pure acid and pure

[1] U. S. Patent 930,967, Aug. 10, 1909.

iron. Commercial sulphuric acid always contains more or less water and other impurities, and in iron also, there is more or less foreign matter. So it may be safely assumed that it will take 1.75 lb. of ordinary commercial sulphuric acid to dissolve 1 lb. of copper and 0.95 lb. of iron to precipitate a pound of copper.

The problem of the commercial treatment of ores by sulphuric acid is, however, much more complicated than the simple process here outlined. If the ore contains foreign elements attackable by sulphuric acid, the acid consumption may be excessive, and if the copper sulphate solution entering the precipitation tanks contains free acid or ferric sulphate the consumption of iron for precipitation will also be excessive.

To determine, therefore, whether any ore may be economically treated by a sulphate process, it is necessary to make a direct test on the ore, and thus ascertain the consumption of acid. The iron for precipitation may be taken, in practice, at 1.5 to 2.0 lb. of scrap iron per pound of copper produced. These factors being known, close approximations can usually be made as to the commercial applicability of the process in its simplest form.

Many improvements on the above simple process have for their basis the cheapening of the solution of the copper, but most of the improvements are based on the precipitation and regeneration of the solvent. If iron is used as the precipitant in the simple process as outlined, the acid is lost, so that new acid has to be supplied to the ore at every cycle of solution. This being the case, sulphuric acid installations may be made at the mine using the sulphide ore for the production of the necessary sulphur dioxide, for the manufacture of acid. The ore, after roasting, may be treated with the acid so produced, to extract the copper, which is in the form of oxide or sulphate and is readily amenable to the process.

Sulphide of copper, in ores, may be converted into sulphate by the action of ferric sulphate, thus:

$$xH_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = CuSO_4 + 4FeSO_4 + S + xH_2SO_4,$$

in which x represents an indeterminate amount of the sulphuric acid. Ferric sulphate has not been used independently for method of extraction on roasted oxidized ores, owing to its slow action. In imperfectly roasted ore its presence may be beneficial by promoting the formation of sulphate from the remaining undecomposed sulphides, should any be present.

Sulphur dioxide, steam, and nitrous fumes have been applied to ore to dissolve the copper as sulphate; this amounts, essentially, to the manufacture of sulphuric acid within the ore mass.

In the application of sulphuric acid for the extraction of copper, cupric oxide, azurite, malachite, and arsenate of copper dissolve readily; phosphate of copper with more or less difficulty. Cuprite (cuprous

oxide, Cu_2O), is not readily soluble, but if moistened with acid and left exposed to the air for some time, it is transformed into the cupric oxide, and is then readily soluble.

According to Schnabel[1] at Stadtberg in Westphalia and at Linz on the Rhine, ores containing 1 to 2 per cent. of copper were sulphated by means of sulphur dioxide steam and nitrous gases, and then leached. At Stadtberg the ores were azurite and malachite disseminated through the quartzose shist, at Linz, at the Stern works, copper carbonates and phosphates. The leaching vessels were tanks of brickwork 3 ft. 3 in. deep. Above the bottom proper these had a false bottom of grating, made of fire brick or other acid proof material, supported by bricks on edge. The ores were piled up on this grating, the gases being conducted underneath it. The gases were respectively generated by roasting iron pyrites in shaft furnaces and zinc blende in muffle furnaces, and by treating Chili niter with sulphuric acid. The sulphur dioxide, nitrous fumes, and steam together formed sulphuric acid which converted the copper compounds into sulphates. After 8 to 10 days the copper sulphate was dissolved out by means of water or of the acid mother liquor left after precipitating the copper. The leaching was so conducted that fresh water or the copper-free mother liquor was allowed to attack the most completely exhausted ore, while the almost saturated solution was run on to fresh ore until is was fully saturated (22 to 26°B). The liquor that drained away ran into receivers, whence it was again pumped on to the ores. This process, which extracted the copper down to 1/4 per cent., has long ago been abandoned. At Stadtberg sulphuric acid was replaced by the cheaper hydrochloric acid as long as the supply of oxidized ores lasted.

Acid Plants at the Mine.—Conditions are frequently ideal for acid manufacture, for leaching purposes, at the mines, if suitable sulphide ore is available. If the mine produces both sulphide and oxide ores, the sulphides may be roasted and the sulphurous gases converted into acid which may then be used to leach both the oxidized and roasted ores. If the sulphide ore is low in sulphur, concentration will usually be necessary to get a material sufficiently high in sulphur to make a gas suitable for sulphuric acid manufacture.

The sulphide ore, or concentrates are usually roasted in a furnace of the McDougal type, and the sulphur dioxide gas passed from the roasting furnace into a series of leaden chambers, where coming in contact with gaseous nitric acid and steam it becomes converted into sulphuric acid. The nitric acid gas is produced by the action of sulphurc acid and nitrate of soda, and passes along with the sulphurous gases into the lead chambers. The combined gases, together with the seam and air, mix in the chambers and condense as sulphuric acid. This is known as chamber

[1] Handbook of Metallurgy, Vol. I, p. 200.

acid and has a specific gravity of about 52°B. and contains about 65.2 per cent. H_2SO_4. The chamber acid, in commercial plants, is then concentrated to 66°B. containing 93.5 per cent. H_2SO_4, and this is the ordinary acid of commerce, or oil of vitriol.

In the manufacture of sulphuric acid, for leaching purposes, the process will be somewhat cheaper than the manufacture of 66°B. acid for commerce, because no purification will be required, and the chamber acid may be used without further concentration. On the other hand, the manufacture of acid for leaching purposes will usually be conducted on a small scale, and hence the cost of operation, per unit of acid, will be largely increased over that of the large commercial plants.

In the manufacture of sulphuric acid, a chamber space of from 15 to 25 cu. ft. should be provided per pound of sulphur burned in 24 hours, and nitrate of soda will be consumed in amounts varying from 3 to 5 per cent. of the sulphur burned.

The cost of manufacturing the acid at the mine will vary within wide limits. The selling price of 66°B. acid, f. o. b. works, in commerical plants, is about $18.00 per ton, but this cannot be made the basis of costs the mine, for the reason that such acid is made under the best possible economic conditions. On the other hand, if acid is manufactured at the mine, assuming the ore to be a sulphide or to contain sufficient sulphides for acid manufacture, there would be no expense for roasting and no expense for sulphur, for in any event, the suphides would have to be roasted, and the sulphurous gases would otherwise be wasted.

Sulphuric Acid Leaching of Oxidized Copper Ores, at Clifton, Arizona.—The Arizona Copper Company have been leaching oxidized surface ores at Clifton, on a large scale, since 1893. The following description of the work was prepared by F. N. Flynn, the Company's Metallurgist.[1]

"Four groups of mines, in the Metcalf District, have contributed this class of ore, but the Metcalf mine has furnished the principal part of the tonnage. The occurrence of the ore, and the method of mining have been described by Mr. Peter B. Scotland, in the *Eng. and Min. Jour.*, July 16, 1910.

"The ores are lowered down the hillside by means of inclined tramways to the railroad bins at Metcalf. Trains of 40-ton, bottom dump cars are hauled over the Coronado Railway, 36-in. gauge tracks, to Clifton, 6.6 miles distant. From the railroad bins, which are common to the various departments of the works, the ore is conveyed by a 30-in. belt to the "Oxide Mill" bin, located near the smelting plant.

"The gangue of the ore partakes of the character of the mine formations—highly altered sedimentary and igneous rocks. The granite-porphyry, quartzite, shale, and limestone have all been more or less altered, resulting in a mass of quartz grains, kaolin, sericite, silicious hematite, magnetite, limonite, garnet and

[1] Private communication from Norman Carmichael, Gen. Manager, Arizona Copper Co., Nov. 1, 1911.

various other silicates of alumina. Fortunately the limestone was completely altered, and the calcium sulphate almost completely removed.

"The copper-bearing minerals, in the order of their importance, are: Malachite, copper-pitch-ore, azurite, impure chrysocolla, cuprite, chalcocite, chalcopyrite, native copper and brochantite. Malachite occurs throughout the upper part of the deposit, and is the all-important mineral. The impure chrysocolla is neither brochantite nor pure chrysocolla. Specimens of this impure mineral, containing 22 per cent. of copper, contain, but 0.05 per cent. of sulphur. The copper is readily soluble in very dilute sulphuric acid without effervescence. Cuprite occurs in the shale, usually unassociated with other copper minerals, except native copper in small amounts. It occurs in very thin flakes, and in such a manner as to suggest its deposit direct from copper sulphate solutions, the latter having been hydrolized by absorption. Chalcocite is found in the porphyry, partly and completely replacing the pyrites.

"The milling ores vary between 2.5 and 3.0 per cent. copper, and analyze about as follows:

SiO_2,	59.0 per cent.
Al_2O_3,	18.0 per cent.
Fe,	9.0 per cent.
Mn,	0.1 per cent.
CaO,	0.1 per cent.
MgO,	0.05 per cent.
S,	1.0 per cent.
Au, Ag, Pb, and Zn,	traces.

About 315 tons of crude ore are treated per day.

The crushing plant consists of:

One 10-in. by 20-in. jaw crusher.

Two sets of 12-in. by 36-in. rolls.

One belt elevator.

One trommel, with 3/4-in. and 5/8-in. holes when new

Water is fed under the first set of rolls.

The 3/4-in. oversize goes to the second set of rolls.

The 3/4-in. to 5/8-in. size is finished product, also the 5/8-in. undersize. Nothing is recrushed. The crushing plant and jigs run 17 hours per day.

"Material between 3/4-in. and 5/8-in. goes to one two-compartment Hartz jig, making top concentrates and tails. The hutch product returns to the ore stream.

"The 5/8-in. undersize, including the crushing water, goes to one five-compartment Hancock jig, making concentrates and tails.

"The concentrates analyze about as follows:

SiO_2,	37.0 per cent.
Al_2O_3	11.0 per cent.
Fe,	22.0 per cent.
Mn,	0.2 per cent.
CaO,	0.04 per cent.
MgO,	0.1 per cent.
S,	5.0 per cent.
Cu,	7.0 to 10.0 per cent.

"The specific gravity of the minerals entering the concentrate runs between 3.76 and 4.63 on sizes larger than 1/8 in. Eighty-five per cent. of the concentrate is larger than eighth inch. From 20 to 25 per cent. of the values are recovered as concentrate, at a ratio of about 10 to 1.

"A belt elevator lifts the concentrates to a bin on the smelter charge floor, from which they are wheeled direct to the blast furnaces.

"The tails bin serves as a dewaterer. The slime water is pumped to settling ponds three-quarters of a mile distant. The slime carries 2.4 per cent. copper and too much soluble alumina to permit of leaching it with the gravel in the present plant. The tailings vary from 1 in. (due to the wear of the trommel) down to the finest sands; 75 per cent. is larger than eighth inch. The tailings are hoisted by inclined skip to a receiving bin, centrally located over the top of the leaching tanks.

"The Joy Mine at Morenci furnishes the pyrite for the manufacture of sulphuric acid. The pyrite analyses:

SiO_2,	9.0 per cent.
Al_2O_3	4.0 per cent.
Fe,	38.0 per cent.
S,	38.0 per cent.
Zn,	2.0 per cent.
Cu,	Variable; usually under 1.5 per cent

The pyrite is crushed to 2 in. The fines are roasted in a Herreshoff five-deck furnace. The coarse material goes to the lump burners. The cinder goes to the blast furnaces.

"The resulting acid is 52° Baume. The capacity of the acid plant is 10 tons per day.

"In the leaching department, small circular wooden tanks are used. There are twelve ore tanks of 13 tons capacity each, or 156 tons total capacity. These have an inner lining of lighter staves. Between the outer and inner staves an acid proof cement preparation is used. The tops of the staves are covered with sheet lead. A false bottom of plank, slightly inclined toward the center, and perforated with holes, serves as a filter bottom.

"The ore (jig tails) is charged to the tank by means of fixed launders overhead, connected with the ore supply bin at the top of the mill.

"The leached tailings are discharged through a circular opening in the bottom of the tank at the center. The opening is closed by means of a wooden plug, extending up through the ore charge, and suspended from chain blocks. The tails are flushed from the ore tanks and hoisted to the railroad bins, from which they are hauled away in 50-ton bottom dump cars. Each ore tank is provided with a belted centrifugal pump for circulating liquors from bottom to top of tank, or to any other tank in the series.

"Ordinary circular wooden tanks are used in the precipitating room. Two square tanks are used for final precipitation. In each of these tanks is a revolving drum or trommel made of cast copper. The circumference is perforated with holes like a trommel. The ends are closed and support the axles. A small door permits charging the trommel with small pieces of wrought iron. The drum is submerged in the solution up to the bearings, and revolves slowly.

The department is arranged on three floors. The top floor for the ore tanks, the middle floor for the precipitating tanks and trommels, and the ground floor for cement copper.

"The ore charge (jig tails) analyze:

SiO_2,	60.0 per cent.
Al_2O_3,	16.0 per cent.
Fe,	8.0 per cent.
Mn,	0.1 per cent.
CaO,	0.06 per cent.
MgO,	0.03 per cent.
S,	0.4 per cent.
Cu,	2.0 to 2.6 per cent.

"In practice three tanks are leached as a unit as regards solutions, although the tanks are charged and discharged singly and at intervals.

"A charge of the solution circulates in each of the three tanks for 4 hours, or 12 hours total time, more or less. In this manner a charge of ore is leached with three strengths of liquor, approximately as follows:

4 hours with 'Strong Liquor.' High in copper and low in acid.
4 hours with 'Weak Liquor.' Lower in copper and higher in acid.
4 hours with 'Acid Solution.'
0.5 hours with Water.
0.5 hours Charging and Discharging.

13 hour cycle.

"Sulphuric acid is added to the resulting wash water, to make the 'Acid Solution,' which in turn makes 'Weak Liquor,' 'Strong Liquor' and 'Copper Liquor.'

"The 'Copper Liquor' goes to the precipitating tanks with a very small fraction of a per cent. of free acid. Usually the free acid is too small to determine.

"The acid consumed in leaching, per pound of pure copper recovered, amounts to 2.6 lb. of 52° B. acid.

"The 'Copper Liquor' from the various tanks is collected in a distributing tank, from which it flows continuously in a small regulated stream to the precipitating tanks. The precipitating tanks are connected in series, and use scrap iron of all descriptions—all of which comes from the works.

"From the last tank in the series the liquor, low in copper, goes to the 'trommel tank' in 'charges.' Small pieces of wrought iron are charged to the trommel. Usually this consists of ties from cotton bales, cut in strips of a foot in length.

"A 'charge' of liquor requires from 10 to 30 minutes in contact with the revolving trommel to complete the copper precipitation. The finished charge containing its cement copper is flushed to settling tanks.

"The decanted liquor, practically free from copper, either in solution or as precipitate, is passed through another set of overflow tanks, containing tin cans, before going to waste.

"The resulting 'Iron Liquor' is pumped to an earthen reservoir, where it soaks into the ground.

"The cement copper, after settling to separate the solution, is accumulated in the patio, and, when sufficiently dry, is moulded into large bricks, by hand. After sun drying for a month, they are sufficiently dry to be fed to the copper converters. The cement copper averages 72 per cent. copper.

"The plant is handled by a superintendent and two white foremen with Mexican laborers. The foremen make frequent mill tests for copper, impurities and free acid. The working strength of all solutions is governed by Baume readings.

"No general rule can be followed for the strength of the various solutions, because the ore is quite variable in composition, both as regards copper and other soluble salts. When ores are met with which show a readily soluble gangue, the acid strength of the solution is reduced from that used or on more silicious ores."

Leaching Plant at the Snowstorm Mine.—At the Snowstorm mine, Larson, Idaho, there has been in operation for some years a leaching plant of 250 tons daily capacity. The ore deposit of the Snowstorm mine consists of disseminations of bornite, chacolcite, and chalcopyrite in certain beds of Revett quartzite. The greater part of the sulphide has however, been oxidized to cuprite, malachite, and chrysocolla. The various prospects are on metasomatic fissure veins carrying chalcopyrite, chalcocite or bornite, with quartz, dolomite, or siderite. In the lower workings of the mine the ore occurs as sulphide, containing only a very small portion of the copper in the oxidized condition, but no attempt has been made to leach the sulphide ore.

The oxidized ores average from 2 1/2 to 3 1/2 per cent. copper, 7 oz. in silver, and $1.00 in gold, per ton. The ore is crushed and run into three agitators, where it is treated with bleaching powder and a 10 per cent. solution of sulphuric acid. By this method chlorine is slowly released, which chlorinates the gold and silver, and to some extent attacks the small quantities of sulphide in the oxidized ores.

The copper solution goes from the agitators through a series of six settling tanks, after which it is precipitated with scrap iron. The residues, containing the silver chloride, are treated with sodium thiosulphate (hyposulphite) to dissolve the silver, and the solution so obtained is passed through settling tanks and the silver precipitated from the clear solution with sodium sulphide. The silver sulphide precipitate is filtered and shipped for refinement. The process is said to save 90 per cent. of the assay value of the ore.

Copper Leaching Plant at the Gumeshevsky Mine, Russia.[1]—The Sissert property, of which the Gumeshevsky copper mine is a part, is one of the largest concessions in the Urals and was originally obtained f working iron ore deposits. As early as 1727 two important copper c

[1] Inst. of *Min. and Met. Bull.*, No. 65; Trans. I. M. M., XIX, 212; Min. In 1910, 210.

posits were discovered on the property. These were worked intermittently for more than 100 years.

The Gumeshevesky mine was shut down in 1871. From old data available it appears that the mine is a contact between limestone and diorite. Oxidized copper ore occurs in a clay formation along the contact where there are old workings, extending about 2 miles in length and possibly 1000 ft. wide. The mine was worked for the oxidized ores only. The deepest shaft is 500 ft. The material raised from the shaft was evidently hand picked and only the large lumps of oxidized ore saved.

The dump consists of clay material with the fine ore that escaped hand picking. It covers an area of about 20 acres, with an average depth of 17 ft. This was thoroughly sampled and estimated to contain 531,000 cu. yd. of material carrying 23 lb. of copper per cubic yard (about 0.79 per cent).

In brief, the process of treatment consists of leaching the crushed material with dilute sulphuric acid, then precipitating the copper from solution with pig iron.

The owners of the property contracted with manufacturers of acid to erect a plant to use iron pyrite from a deposit about 4 miles from the dumps, and to sell to them, during a period of 10 years, 53°B. acid at $4.32 per long ton (0.19 cents per pound). The contractors were to extract the copper from the pyrite paying the estate a royalty of $145 to $175 per ton of copper produced, and were bound to burn 4000 to 4800 tons of pyrite annually. The pyrite was estimated to contain 3.5 to 8.0 per cent. Cu, and the contractors were required to leach it so as to leave no more than 0.2 to 0.3 per cent. copper in the tailings.

The method used for the extraction of the copper from the burned pyrite consists in roasting it in a muffle with the addition of sulphuric acid at a temperature of 450 to 550° C. This brings the copper into soluble condition. The product is then leached in lead-lined wooden tanks, first with water, then with barren acid solution left after precipitating the copper on iron plates, and finally with dilute acid. The copper is precipitated from the solution at boiling temperature, on cast iron plates. In this work 2 lb. of acid and from 1 to 2 lb. of iron are used per pound of copper extracted.

The oxidized dump material is composed of one-third large pieces needing grinding and two-thirds of fines. It is of the following average composition; SiO_2, 37.0 per cent.; Fe, 19.6; Al_2O_3, 20; CaO, 0.25; Cu, 0.75 per cent.

The ore is shoveled into side dump cars and hauled by horses to the end of an inclined troughed belt conveyor which raises it to the top of the crushing plant. Here it is wet crushed in a breaker and Chili mills to yield a pulp containing 33 per cent. dry solids and having 50 per cent.

material fine enough to pass through a 136-mesh screen. This pulp is conducted by wooden launders to the leaching vats. Fig. 45 represents a general plan and section of the leaching and precipitating plant. This consists first of 10 leaching tanks 184×42×6 1/2 ft. deep. These tanks are erected on a rock foundation, and have masonry walls, covered with 4 in. of concrete, then 1 in. of reinforced asphalt. The asphalt covering has lasted successfully for 2 years and has been subjected to temperatures from −40 to 102° F. The plant is operated in the warmer months only.

Each leaching tank is charged in 8 hours with pulp containing 200 tons dry material. The pulp during this time receives 13.2 tons of 53°B.

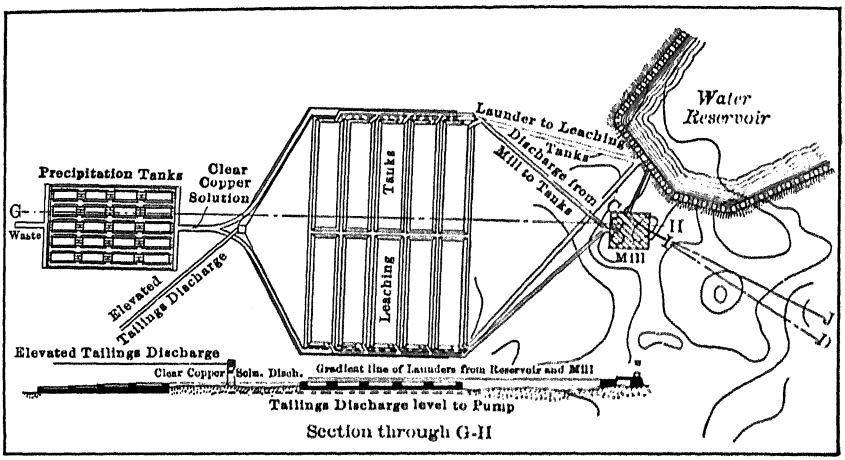


FIG. 45.—Copper leaching plant at the Gumeshevesky Mine, Russia.

sulphuric acid which is run into the tank, after which the stirring arms of an agitator are lowered into it. This machine is furnished with five vertical shafts, each having a stirring arm at its lower end. The agitator is moved from end to end of the tank and stirs the pulp for 9 hours. The material in the tank is then allowed to settle, the clear solution is decanted through the launders to the precipitation tanks. Wash water is run in to fill the tank, the pulp is again agitated for 4 hours, allowed to settle, and the solution decanted as before. Four washes and decantations are thus made. The tank is provided with a side door through which the tailings are discharged, while they are kept in suspension by means of the agitator. Care must be taken to add sufficient water to make at least 2 1/2 parts of water to 1 of tailings. The tailings go to a centrifugal pump which raises them to the elevated tailings discharge. It takes 3 1/2 hours to discharge a tank. The agitator is then transferred by a crane to another tank. The cycle of the leaching operation requires 5 days, two tanks being charged and two discharged daily.

The quantity of solution decanted at one time is 660 tons. The copper content of the solution varies from 0.121 per cent. Cu at the first decantation to 0.015 per cent. in the last wash. About 50 per cent. of the copper is extracted by these leaching operations, the insoluble balance consisting of copper silicate and native copper.

The accompanying table shows the actual consumption of acid as compared with laboratory tests.

CONSUMPTION OF ACID

Acid consumed by	Laboratory tests, per cent.	Actual practice, per cent.
Copper	22.5	25.0
Alumina	49.9	50.0
Iron oxides	12.4	15.0
Lime	4.2	10.0
Organic matter, etc	11.0	

There are 20 asphalt lined concrete precipitating tanks arranged in five rows with four tanks per row. Each tank is 43 ft. long, 19 ft. wide, and 2 ft. 7 in. deep. The upper tank of each row is filled with 110 to 120 tons of cast-iron plates. The other four have inclined false bottoms, each covered with about 3 tons of granulated cast iron in a layer 4 in. thick. Thus there are in all the tanks 460 tons of plates and 200 tons of granulated iron. The solution flows through the system at the rate of nearly 200 tons per hour. The average entering solution contains 0.04 to 0.07 per cent. Cu, and when leaving it contains 0.002 per cent., indicating a precipitation of 95 per cent. of the copper. The tanks containing the plates are charged at intervals of 3 weeks; the other tanks every 4 to 8 days. The plates are cleaned by scraping and washing off the loosely adherent copper. The cast iron granules are washed with water in a trommel perforated with 1/8-in. holes. The under size of the trommel, consisting of cement copper and small grains of iron, goes to a magnetic separator where the iron is removed. The oversize of the trommel is returned to the tanks. Granulated cast iron is in every respect a more convenient precipitant than cast iron plates, bars, or scrap iron. Twelve tons of granules have the same precipitating capacity as 120 tons of plates. It takes eight men 45 hours to clean 120 tons of plates, as compared with six men taking care of 12 tons of granules in 8 hours.

The iron consumed is 1.8 to 2.0 tons per ton of copper recovered. The cement copper, containing 60 to 75 per cent. of the metal, is treated by melting in a reverberatory furnace, adding to it a small quantity of matte of the grade of white-metal to remove impurities. The resultant

blister copper is then rabbled and poled in the usual way to produce a brand of best-selected metal.

The accompanying table, based on operations for 13 days in June, 1909, gives an idea of working costs under normal conditions.

OPERATING COSTS OF COPPER LEACHING PLANT IN THE URALS

Item of expense	Total cost	Cost per ton of dump material	Cost per lb. of copper
Wages and superintendence	$1813.14	$0.238	$0.024
Supplies	289.65	0.037	0.004
Assay office expense	51.51	0.007	0.001
Repairs and renewals	736.06	0.099	0.010
Power	210.56	0.027	0.003
Acid, 351 tons at $4.32	1516.32	0.196	0.020
Pig iron, 62.45 tons at $10.48	676.95	0.088	0.009
Refining, 33 tons at $12.50	412.50	0.053	0.006
Tax on 33 tons at $15.96	526.68	0.068	0.007
Depreciation and general expenses	2218.32	0.290	0.031
Total	$8481.69	$1.103	$0.115

From 7735 tons of crushed dump material, 33 tons, or 0.43 per cent. of copper, was recovered, using 341.1 tons of 53° B. sulphuric acid and 62.45 tons of pig iron. The cost of the plant, not including the acid works, was $128,700.

Ferric Sulphate, $Fe_2(SO_4)_3$.—If cupriferous pyrites is treated with a solution of ferric sulphate, copper goes into solution in proportion to the quantity of iron that has been reduced from the ferric to the ferrous condition. If ferric sulphate is applied to a fresh lot of cupriferous pyrites it is at first quite rapidly reduced, and the richer the mineral in copper, the quicker and more perfect will be the reduction. As the copper content in the ore is diminished, the reducing action becomes slower, and in the later stages of treatment, if the ferric sulphate solution is allowed to remain in contact with the partially exhausted ore until reduction has taken place, it will be found, (1) that the free sulphuric acid is on the increase, and (2) that the copper content of the solution does not increase in proportion to the quantity of ferric sulphate reduced, as is the case when it is first applied to untreated ore. On continuing the treatment until the reduced liquor shows no furthur increase in its copper content, the proportion of free acid rapidly increases, due to the action of ferric sulphate on iron pyrites. At a slightly elevated temperature the leaching action of the mineral is more rapid.

Before the copper is precipitated with iron, precautions should be taken to insure as far as possible the reduction of the ferric sulphate, or the consumption of iron will be excessive and the precipitation retarded.

S. R. Adcock carried out at Rio Tinto a series of experiments[1] to determine the amount of copper that could readily be extracted from cupriferous pyrites by washing the mineral with a solution of ferric sulphate, and also to note the changes that take place during the operation. To this end varying quantities of crude smalls, all of which would pass through a 0.25-in. sieve, were washed in small lead tanks with a cold solution of ferric sulphate (2 per cent. Fe); the liquor was allowed to remain in contact with the mineral until its color indicated that the greater part of the iron had been reduced, when it was drawn off and a fresh quantity of ferric sulphate added.

These experiments show how rapidly ferric sulphate solutions act upon the cuprous sulphide in the pyrites, and in places where these liquors are plentiful or can be cheaply manufactured they no doubt could be used to advantage for extracting say one-half of the total copper content of mineral running from 1.5 per cent. and upward, before it is formed into heaps for treatment by the open air or weathering process. The extraction by this process compares favorably with the (1) open-air calcination, until recently so extensively used at Rio Tinto and the (2) "weathering" or air oxidation process.

"The amounts of copper extracted at different periods were calculated from the analyses of the liquors, and the results obtained from these experiments are given in the following table:

Weight of mineral treated	Copper content	Days under treatment	Copper extracted
5 kg.....	4.62 per cent.	3	31.90 per cent.
		8	44.00 per cent.
		23	61.00 per cent.
		31	66.00 per cent.
5 kg.....	1.62 per cent.	4	23.00 per cent.
		13	38.00 per cent.
		66	50.50 per cent.
		94	60.00 per cent.
2 kg.....	6.49 per cent.	30	50.70 per cent.
		61	63.30 per cent.
		180	79.00 per cent.

"The open-air calcination as applied to 2.5 per cent. Cu mineral yields three-fifths of the total copper (60 per cent.) which is at once dissolved out after calcination.[2] The weathering method yields 88 per cent. of the total copper content of the mineral treated in 6 years.[3] While carrying out the above trials it was noticed in each case that, after the first two or three washings, the liquors gradually increased in their free acid content, and further experiments were performed

[1] Min. Ind., Vol. IX, 1901.
[2] J. H. Collins, Trans. Inst. Min. and Met., Vol. II.
[3] J. H. Brown, *Jour. Soc. Chem. Ind.*, Vol. XIII.

to determine the chemical action that was taking place. To determine the action of ferric sulphate on cuprous sulphide, 20 grm. of pure copper glance (Cu_2S) crushed to a fine powder, was treated with an excess of the ferric solution. On filtering off the liquor, well washing the insoluble residue, etc., it was found on analysis that 15.39 grm. of copper had been dissolved, 27.43 grm. iron has been reduced from the ferric to the ferrous condition, and 3.83 grm. of free sulphur had been produced. Based on these results it will be seen that the following equation represents the reaction that has taken place:

$$(1)\quad Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S,$$

but having noticed on every occasion when carrying out experiments on the above lines, that the first 50 per cent. of the copper is more easily extracted, it is probable that the reaction is more correctly shown as taking place in two stages, thus:

$$(a)\quad Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4.$$
$$(b)\quad CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S.$$

"With a view to determine the action of ferric sulphate on iron pyrites FeS_2, 100 grm. low grade ore which had been previously ground to a fine powder, sampled and analyzed, was washed with a strong solution of ferric sulphate (2 per cent. Fe) until the analysis of the liquor drawn off from time to time showed that practically all the copper had been removed. The washed mineral was then treated for 63 days with the ferric solution, and at the end of this period it was noticed that the reduction of the ferric iron was taking place almost as rapidly as at the commencement of the experiment. From the analysis of the washings, which were drawn off when the color indicated that reduction had taken place, it was noted that each successive wash showed a slight increase in its free acid content until the copper contained by the mineral had been practically exhausted; at this stage the free acid appeared to have reached its maximum, and from thence was always found present in quantity, directly proportional to the amount of ferric sulphate that had been reduced by the mineral.

The mineral at the conclusion of the experiment was well washed with distilled water, and dried at 100° C. The following are the analyses before and after treatment:

Components	Before	After
Copper	0.64 per cent.	0.07 per cent.
Sulphur	51.20 per cent.	33.09 per cent.
Iron	43.82 per cent.	44.60 per cent.
Arsenic	0.56 per cent.	0.21 per cent.
Antimony	0.03 per cent.	0.02 per cent.
Bismuth	0.003 per cent.	0.002 per cent.
Lead	0.97 per cent.	1.10 per cent.
Zinc	2.00 per cent.	0.12 per cent.
Silica	0.39 per cent.	0.46 per cent.
Total	99.613 per cent.	99.672 per cent.
Free sulphur	Nil	2.51 per cent.

"The above analyses show that the copper and zinc originally contained by the pyrites are almost totally extracted by ferric sulphate, the arsenic to a lesser extent in the same time, while all the lead remains in the washed material, probably as insoluble sulphate. It is well to note that there is free sulphur present in the material after treatment.

"The results of the analyses of the liquors obtained by washing the mineral for 63 days, after the copper had been extracted, were as follows: During this trial the liquors were kept at a slightly elevated temperature; 45.2 grm. of ferric iron reduced to the ferrous state; 44 grm. free sulphuric acid formed, and 4.2 grm. of iron (from the pyrites) dissolved. Based on these results it is probable that the following equation represents the action of ferric sulphate on iron pyrites:

$$(2)\quad 11Fe_2(SO_4)_3+2FeS_2+12H_2O=24FeSO_4+12H_2SO_4+S.$$

"The amount of pyrites required to effect the reduction is very small, but the reaction in the cold is slow in taking place, unless a large excess of mineral is exposed in proportion to the quantity of ferric sulphate to be reduced; at a temperature of from 50 to 60° C. the reaction takes place much quicker than at ordinary temperatures."

Ferric sulphate also reacts with cupric oxide, according to the equation:

$$(3)\quad 3CuO+Fe_2(SO_4)_3=3CuSO_4+Fe_2O_3,$$

and somewhat similarly on the carbonate, with the liberation of CO_2.

Zinc in its sulphide combination is readily soluble in a solution of ferric sulphate, according to the equation:

$$(4)\quad ZnS+Fe_2(SO_4)_3=ZnSO_4+2FeSO_4+S.$$

From equations 1, 3, and 4, it is readily estimated that theoretically, 6.3 lb. of anhydrous ferric sulphate are required to dissolve 1 lb. of copper from its cuprous sulphide combination, and 2.1 lb. from the cupric oxide: 6.1 lb. of ferric sulphate is destroyed in dissolving 1 lb. of zinc from sphalerite, and as zinc is more electropositive than iron, it will not be precipitated by it, but will accumulate indefinitely unless some means is provided to remove the zinc sulphate, or at intervals renew the solution.

Experiments with Ferric Sulphate at Cananea.—W. L. Austin gives an account[1] of experiments carried out at Cananea, State of Sonora, Mexico, by the Cananea Consolidated Copper Co., from the original notes furnished by David Cole, assistant general manager of the company, with a view to ascertaining the leaching qualities of local material. While these experiments did not lead to the adoption at Cananea of the method advocated, the results obtained are instructive and of practical value to any one contemplating similar experimental work.

"The material treated at Cananea consisted of mill-tailing sands and of flue dust from the furnaces. The leaching was done by simple percolation without agitation. The copper was precipitated from the cuprous liquors by means of

[1] "Mines and Methods," Sept., 1910.

metallic iron. The spent solutions were regenerated by forcing heated air through them. The principal difficulties encountered arose in the regeneration of the liquors.

"There is from 0.27 to 0.66 per cent. zinc in the mill-tailing sands at Cananea and the copper varies from 0.54 to 0.89 per cent. It was found that the zinc minerals were more readily attacked than those carrying the copper, for in the same time that approximately 65 per cent. of the copper was extracted 72 per cent. of the zinc went into solution. It was thought at Cananea that dilution of the solutions by wash water introduced to remove the soluble copper salts from the tails before allowing them to go to waste would suffice to keep the zinc content in the solution low enough to prevent serious fouling. A certain proportion of the zinc salts would be removed in this manner because the wash water after flowing over iron to deposit the copper would be allowed to escape, but the effect of zinc salts in the application of the process in any particular case can only be determined by experimenting with the ore in question on a considerable scale. In using 2 lb. solution to 1 lb. of ore it was found that 94 per cent. of the soluble matter is extracted without increasing the bulk of solution with wash water.

"Only very small amounts of alkalis went into solution in treating the sand tailings—about 0.1 per cent.—and the quantities of alumina and lime were negligible. The pyrites in the ore was found to reduce the ferric salts, causing a waste of the solvent.

"It was found that the average loss of ferric sulphate per pound of copper extracted was 4.37 lb. This figure was derived by crediting the gain in ferrous sulphate from both the action of the ore and from the precipitation of the iron, and 'calculating the oxidation in the tower.'

"It was found at Cananea that a ferric sulphate solution accomplished a very complete extraction of the copper from material containing the oxides and carbonates, but that it acted more slowly upon those carrying the metal in the form of chalcocite. Chalcopyrite was hardly attacked at all. The content of the solution in ferric sulphate was found to be of comparatively small importance provided base salts were absent. It worked when it carried as small an amount of ferric salt as 1 per cent., and the extractions were nearly as complete when using 2 per cent. solution of ferric sulphate as when using 7 per cent. A freshly precipitated solution acted more energetically than an old one, even though relatively weaker. The presence of much basic sulphate was found to greatly retard the leaching, 'clogging' the action. For this reason the solution was settled in the oxidizer before using. About 65 per cent. of the copper contents of the mill-tailing sands could be extracted in about three hours when the liquor was boiled, or in about 7 hours when it was kept at a temperature of 70°.

"Concentrates gave about 40 per cent. extraction.

"After the liquors were thought to contain a sufficient quantity of copper in the sulphate form they were conveyed to the precipitating tanks where the metal was removed by being brought in contact with metallic iron:

$$(5)\quad CuSO_4 + Fe = FeSO_4 + Cu.$$

"The consumption was light because when the solution is hot the precipitation is very rapid and complete.

"After the liquors had passed through the precipitating boxes the iron was

practically all in the ferrous condition and it became necessary to regenerate the solvent—that is, to reoxidize the iron—before it would again be available. It is precisely in the regeneration of the spent solutions that the weakness of leaching methods based on the use of ferric salts becomes apparent.

"At Cananea the regeneration was effected by pumping the solution into an oxidizing tank where it was heated by a steam coil and agitated and oxidized by hot air. The capacity of the oxidizer was 30,000 lb. of solution; the working height of the column was 11 ft. 8 in. It was thought that 18 ft. would give better results. From the oxidizer the solution was led to a settler and from which the clear liquor was drawn off to a feed tank. It was then available for leaching.

"The reactions which take place when an attempt is made to oxidize ferrous sulphate to the ferric condition, without the presence of free acid, are very complicated. Basic ferric salts, of which there are many varieties, invariably form and are precipitated, thereby causing the loss of a large part of the iron unless free sulphuric acid has been added in the amounts necessary to produce the neutral ferric sulphate. For the purpose specified (the formation of neutral ferric sulphate), ten parts of ferrous sulphate require two parts of concentrated sulphuric acid. The reactions which occur in the transformation are indicated by the following equation:

$$(6)\quad 2(FeSO_4)+H_2SO_4+O=Fe_2(SO_4)_3+H_2O.$$

"If a solution of neutral ferric sulphate is heated with ferric hydrate, there results a deep brown liquor containing a more basic salt—two-thirds as much sulphuric acid combined with the same amount of iron as in the neutral salt. This basic salt is also formed when a solution of ferrous sulphate is slowly oxidized by contact with the air, while at the same time a still more basic salt is produced (with one-sixth as much sulphuric acid as is present in the neutral sulphate), together with other soluble sulphates and the neutral ferric sulphate.

"The basic salt containing two-thirds as much sulphuric acid as is present in the neutral sulphate, is decomposed by heating, or by dilution of the solution, the resulting products being neutral ferric sulphate and a yellow precipitate containing the one-sixth salt referred to above. These two last named ferric compounds predominate when a solution of ferrous sulphate is oxidized by exposure to the air, and are claimed by some authorities to be the final products from the oxidation described.

$$(7)\quad 10(FeSO_4)+O_5=3(Fe_2(SO_4)_3)+Fe_4SO_9.$$

"From the above equation it is evident that in converting a ferrous into a soluble ferric sulphate by oxidation in the air, with the assistance of heat, without the addition of free acid, 40 per cent. of the iron is deposited in the form of insoluble basic ferric sulphates and is therefore lost as an active reagent for the required purposes, in addition to a loss of the acid with which it is combined. Hence in order to keep up the grade of the solvent in leaching with ferric salt, it becomes necessary to constantly replenish the acid constituent of the compound, the latter being the reagent consumed, and the process becomes virtually one of leaching with sulphuric acid. Where a heavy iron sulphide is calcined before leaching, the loss of iron becomes of comparatively small importance, but where the ferrous salt is an item of expense, the cost is considerable. If 10 lb. of ferrous

sulphate are required to carry out a certain leaching operation, 4 lb. will be lost in the process of regeneration by aeration, unless 2 lb. of concentrated (66° B.) sulphuric acid is added to the solution to prevent the iron from taking the form of a basic salt. Therefore, in estimating the cost of leaching a given ore, the relative expense in providing free acid, as against that for ferrous sulphate, has to be considered.

"From the above remarks, it is apparent that the reactions which take place in the regeneration of the spent solutions by the methods used at Cananea are too complicated to be written down in formulæ; the actual figures disclosing results obtained are more illuminating.

"In making the ferric solution employed at Cananea the ferrous sulphate used contained sulphide impurities which caused some irregularities during the oxidation, the ferric sulphate being destroyed. The sulphides might have been removed by dissolving the sulphate in a separate tank and decanting the clear solution. The ferrous salt was added to hot water into which had been pumped some ferrous solution and the whole was heated by means of a steam coil near the bottom of the oxidizing tank. Air was forced in by a compressor after passing through a heater where is attained a temperature of from 200 to 400° F. and served to agitate and oxidize the solution.

"After it was apparent that the ferrous salt had gone into solution, samples of the liquor were taken which gave the following results:

Sample No.	Hours	Ferrous sulphate per cent.	Ferric sulphate per cent.	Ferrous sulphate pounds	Ferric sulphate pounds	Temperature degrees C.
1	0	12.1	1.6	3630	480	76.0
2	1	11.7	2.1	3510	620	79.0
3	2	11.3		3390		79.5
4	4	10.9		3270		80.5
5	5	10.5		3150		80.5
6	6	10.5		3150		81.5
7	8	9.4		2820		81.0
8	24	6.5	5.6	1950	1580	79.0
9	26	6.1		1830		79.0
10	28	5.8		1740		79.0
11	30	5.5	6.6	1650	1980	77.0
12	32	5.1	7.0	1530	2100	77.5

Total ferric sulphate formed in 32 hours was 2100−480=1620 lb. Average ferric sulphate formed in 1 hour=50.6 lb.

"The table shows no oxidation in the solution between the fifth and sixth samples. A possible explanation of this feature is that ferric sulphate attacked the sulphide of iron already referred to as an impurity in the ferrous salt fed to the oxidizing tank.

"A basic sulphate which formed in the tank during the process of oxidation is said to have interfered to a great extent with the operation.

"In the test from which the above results were obtained, 300 lb. sulphuric acid were added after the solution had been oxidizing for 28 hours. Four hours later a valve leaked and the solution in the tank had to be drawn off, so that it was thought that the basic sulphate may not have received the full benefit of

the acid. The iron sulphides in the solution were considered to have retarded oxidation to a marked extent.

"At Cananea the oxidation of the ferrous to the ferric sulphate was found to be a serious problem as the transformation was very slow, and it was thought that a successful application of the process will depend more on a satisfactory solution of this feature than on any other.

"In an experiment made previous to the one mentioned, before alterations had been made in the oxidizing tank, 6.4 tons of solution were treated for 2 days. During that interval 1,500,000 cu. ft. of air at a temperature of about 140° C. (equivalent to about 100,000 lb.) were forced through the solution with the following results:

	Ferrous sulphate		Ferric sulphate	
	Per cent.	Pounds	Per cent.	Pounds
Before blowing	6.80	870.4	0.82	104.9
After blowing	5.40	691.2	1.80	230.4

"It is stated that only 125.44 lb. of ferric sulphate were formed, which also included the precipitated basic salts. If all the oxygen in the air had been utilized, nearly 200,000 lb. ferric sulphate might have been produced had the necessary amount of ferrous solution been available. It took 1200 times more air than was theoretically necessary to produce the results desired.

"In order to increase the efficiency of the oxidizer, perforated discs were submerged in the solution and heated air from the compressor was forced in at the bottom. The improved oxidizer gave much better results than were obtained with the former one.

In making an estimate of the expense of converting the ferrous solution at Cananea, no account appears to have been kept of the ferrous salt, nor of labor and repairs; only the following items are given:

Steam for heating the solution through lead coil,	$3.80
Power used for compressor,	0.85
Coal to heat the air, 262 lb.	1.05
Sulphuric acid, 300 lb.,	2.00
Total,	$7.70

"These figures are for 24 hours' run. The sulphuric acid is taken at $0.0066 per pound, at which price it was thought that probably it could be manufactured at Cananea.

"As the average amount of ferric sulphate formed in the oxidizer was 50.6 lb. per hour, dividing the $7.70 by 24 to obtain the cost per hour, and dividing this result by 50.6 to get the cost per pound, gives $0.0063 as the cost of 1 lb. of ferric sulphate produced in the manner described.

"An estimate made by the engineers who conducted the tests at Cananea is given below. These figures are said to represent the actual results obtained in

treating a 10-ton lot of Cobre Grande ore. This ore contained 3 per cent. copper, and the extraction is said to have been 96 per cent.

	Per ton	Per cent.
Crushing to six mesh,	$0.50	13.4
Roasting,	0.50	13.4
Oxidizing,	0.95	25.5
Acid, 16 lb. at 1/2 cent,	0.08	2.1
Coal to evaporate wash water,	1.00	26.8
Iron to precipitate copper,	0.30	8.0
Heating solution,	0.20	5.4
Labor,	0.20	5.4
Total,	$3.73	100.00

"This is equivalent to $0.064 per pound of copper. It was found in this experimental work that the best leaching results were obtained when the copper was in the oxidized condition. A test made on 1735 lb. of flue dust containing 5.63 per cent. copper was satisfactory, as shown below.

"The dust was first calcined to oxidize the sulphides and then leached with a hot solution of ferric sulphate. The leaching proceeded rapidly; two applications of the solution left practically no copper in the tailings. The following table shows the consumption of ferric sulphate in this operation:

	Pound.
Ferric sulphate ($Fe_2(SO_4)_3$) in feed solution,	440
Ferric sulphate ($Fe_2(SO_4)_3$) in tail solution,	190
Ferric sulphate ($Fe_2(SO_4)_3$) used to leach,	250
Copper in charge,	97.5
Copper in solution, 95 per cent. extraction,	92.6
Ferric sulphate consumed per pound of copper extracted,	2.7

The time factor was ignored in this test, the perfection of the leach alone being considered. The dust contained about 30 per cent. iron so that an excess of ferrous sulphate was found in the tail solution. No attempt was made at estimating the cost in these tests because the expense for calcining, labor, steam to heat the solutions, repairs, etc., could not be accurately obtained.

"Another test said to have been made on a 10-ton lot of flue dust assaying 7.5 per cent. copper, resulted in an extraction of 94 to 96 per cent. The cost items were given as follows:

	Per ton	Per cent.
Calcining,	$0.50	12.0
Oxidizing,	1.44	34.5
Acid, 16 lb. at 1/2 cent,	0.08	1.9
Iron for precipitating the copper,	0.75	18.0
Steam for heating solution,	0.20	4.8
Coal for evaporating the wash water,	1.00	24.0
Labor,	0.20	4.8
Total,	$4.17	100.0

Cost per pound of copper, $0.029.

"The Cananea tests appear to have come to a sudden termination through the breaking down of the oxidizer, without the cost of the solvent having been conclusively established. The extraction was apparently satisfactory.

"The figures given in the foregoing, relative to the cost of producing the ferric sulphate are either based upon what might have been accomplished with a perfect oxidizer, or are incomplete, or are theoretical deductions from imperfect results. They are not conclusive.

"It is to be regretted that having carried the work along to the point reached, an effort was not made to definitely ascertain the cost of producing the solvent, or what is the same thing, the expense of regenerating the solutions.

"An estimate made by an engineer in the early stages of the experiments as to the probable cost of producing copper by this method is given below. This estimate was figured before improvements in the oxidizer were made. No charges are included for mining, transportation, crushing, calcining, general expenses, etc.

COST OF TREATING SANDS YIELDING EIGHT POUNDS OF COPPER PER TON

	Per ton sands	Per pound copper	Per cent.
Coal to heat air	$0.57	$0.0713	27.6
Power, at $0.65 per horse-power day for blowing air	0.12	0.0150	5.8
Acid—if made on ground—2 lb. acid per 1 lb. Cu	0.08	0.0100	3.9
Iron, 12 lb. at 1 cent. per pound	0.12	0.0150	5.8
Labor and maintenance	0.60	0.0750	28.9
Shipping and refining at $0.05 per pound copper	0.40	0.0500	19.3
Added for waste of material, 20 per cent. of $0.89	0.18	0.0225	8.7
	$2.07	$0.2588	100.0

"A summary of the cost of producing the ferric sulphate used in the experiments at Cananea, derived from independent sources, is given below. The figures include only steam heat, heat for air, power for compressor, and acid.

COST OF FERRIC SULPHATE

	Lb. ferric sulphate consumed per pound of copper		Ferric sulphate cost of 1 lb.	Ferric sulphate cost per pound of copper	
	Oxides	Sulphides		Oxides	Sulphides
I	2.5	3.3	$0.004	$0.01	$0.013
II	2.7		0.0064	0.017	
III		4.37	0.0226		0.099

"The cost per pound of ferric sulphate in No. II is probably the closest approximation to the actual cost of the pound of ferric sulphate made at Cananea, but does not include original cost of the ferrous sulphate, losses in handling, basic salts, nor losses from presence of impurities."

Thomas' Experiments with Ferric Sulphate on Sulphide Ore.[1]—F. Thomas experimented with ore of the following composition:

SiO_2, gangue,	44.7 per cent.
Cu_2S (10.5 per cent. Cu),	13.5 per cent.
Fe_2S_3,	25.25 per cent.
Fe_2O_3,	5.76 per cent.
MnO,	0.18 per cent.
Al_2O_3,	7.5 per cent.
P_2O_5,	0.34 per cent.
CaO,	2.83 per cent.
Traces, Sb, Sr, Mg, and K.	

The principal results of his experiments are as follows: The double sulphides of copper, which occur in nature, require for their complete transformation by means of ferric sulphate such a long treatment and so fine crushing, that a commercial application of this method of leaching does not pay under the conditions existing in most copper producing countries. Copper-iron sulphides, artificially prepared, also resist the action of ferric sulphate in the same way as the natural ones. Free copper sulphides and oxides react with ferric sulphate in aqueous solution easily and quickly. The reason to which the difficulty of the action of ferric sulphate in the former cases is due must, therefore, lie in the chemical affinity between the ingredients of the natural and artificial sulphur ores in copper. The presence of a larger quantity of ferrous sulphate in the solution impairs the solution of copper from cuprous sulphide by means of ferric sulphate. The method suggested in the Siemens-Halske process for roasting copper ore, so that the main quantity of the iron is transformed into oxide while the main quantity of copper remains as cuprous sulphide, is practically impossible. Neither can satisfactory results be obtained by means of dead-roasting of sulphide ores, for the reason that at the temperature required for this purpose basic silicates are formed by means of combination of the copper oxide with the silicates of the gangue, and that perhaps also salts of the Fe_3O_4 type are formed by the combination of the oxides of copper and iron; such salts are acted upon very slowly by ferric sulphate. The double sulphides must therefore be destroyed by oxidizing roasting at so low a temperature that the formation of the compounds just mentioned is impossible. This temperature is about 450 to 480° C. The product thus obtained contains the copper essentially in the form of sulphate. The low temperature of roasting permits the use of simple furnaces, and a crushing of the ore is sufficient, corresponding to 484 meshes per square centimeter. The leaching can be so conducted that a solution of copper sulphate is obtained with only small quantities of iron.

[1] *Metallurgie*, Jan. 15, Feb. 8, and 22, 1904.

Experiments in Southern Tyrol, Spain.[1]—A copper plant was erected in Southern Tyrol, in which an attempt had been made to employ the old Siemens-Halske process, the first stage of which is leaching with ferric sulphate solution. This preliminary leaching was a failure, so that the subsequent electrolytic precipitation of the copper was never attempted. The reason was that the ore contained the copper in the form of the compound Cu_2S,FeS,FeS_2; this was roasted at such a high temperature that the copper oxide combined with other oxides and formed combinations like CuO,Fe_2O_3 and silicates, which are not amenable to leaching. The ore was afterward roasted at a low temperature, which was then easily leached, and it was decided to work the copper ore simply for copper sulphate.

Copper Extraction at Kedabeg, Russia.[2]—The rich ores at Kedabeg are smelted. The lean ores, containing less than 5 per cent. copper, say 3 per cent., and which consequently would not bear the cost of direct smelting, are treated by leaching. The process is very simple and well adapted to the local conditions which scarcely permit of the use of salt or other decomposing reagents. The ore is cheaply roasted in kilns or Gerstenhofer furnaces without fuel, the copper being thus brought into soluble form for leaching. This presents no great difficulty, as the copper, originally existing as sulphide, is oxidized partially to sulphate in the furnace, the sulphatization being completed to a certain extent later during the leaching by the ferric sulphate formed in the roasting and also present in the residual solutions from the electrolytic precipitation, the latter being run into leaching ponds. A comparatively long time is required to obtain a practically complete change of the copper to sulphate, several years' leaching being necessary to reduce the copper contents to 0.5 or 0.7 per cent. copper. However, from 50 to 70 per cent. is obtained at a very small cost in the first year. The whole plant is in the open, without covering or roofing, and on sloping ground. The ground, very impermeable to begin with, is completely hardened by the decomposition of basic salts of iron.

The copper is precipitated in wooden tanks by means of scrap iron, a rapid circulation being kept up all the time. In this way 409.5 metric tons of cement copper, with 65 to 75 per cent. Cu, are produced per annum.

The Millberg Process.[3]—Well roasted copper pyrites or copper cinders contain copper as:

1. Copper sulphate, soluble in water.
2. Copper oxide, soluble in ferric sulphate.

[1] W. Borchers, *Metallurgie*, Aug. 8, 1909.
[2] Gustave Kolle, Min. Ind., Vol. VI.
[3] *Chemicker Zeitung*, XXX, 511.

3. Cuprous oxide, capable of being oxidized by ferric sulphate which will then dissolve it.

4. Copper sulphide, oxidizable by ferric sulphate which will then dissolve it.

Millberg's method consists in leaching the roasted ore or cinders with a solution of ferric sulphate by which the copper is salts are dissolved out and pass into the filtrate. This filtrate will then contain ferric sulphate, ferrous sulphate, copper sulphate and sulphate of other metals when present, such as zinc, manganese, cobalt, nickel, and aluminum. Ferric sulphate is very effective in bringing the copper salts into solution so that in burnt pyrites containing 0.8 per cent. to 4.0 per cent. copper, there is left in the residues 0.05 per cent. to 0.2 per cent. only.

The filtrate contained in a tank is brought to the temperature of 60° C. and to it is added a little ferric sulphate solution till by testing with ferrocyanide solution the end point is reached. This may be, for example, 0.66 per cent. of a ferric sulphate solution of 25° B. This oxidizing action will not exceed 2 days, and for some kind of cinders but a few hours. Air is then blown into the solution in presence of an alkali base, such as milk of lime. The ferric sulphate is precipitated as an insoluble basic sulphate. This is filtered or decanted off and there remains in the filtrate the sulphates of copper and other metals.

The solution is heated to the boiling point, and to it is slowly added dilute milk of lime, which precipitates the copper as an insoluble basic sulphate of a light green color and leaves the other sulphates in solution. The precipitation must be watched and the treatment stopped as soon as the copper has been precipitated.

The Elliott Process.[1]—The Elliott process consists, essentially, in leaching the ore with a hot non-acid solution of ferrous sulphate, passing air through the solution during the operation of leaching, precipitating the copper from the solution with iron, thereby regenerating the ferrous sulphate for a repetition of the process.

The process is applicable to oxidized ores; if the ore to be treated is a sulphide, it has to be given a preliminary roasting to convert the sulphide into the oxide or sulphate. The air, preferably heated, converts the ferrous sulphate to the ferric sulphate, which then acts on the copper oxide. The oxidation of the ferrous sulphate to ferric sulphate may be expressed:

$$6\,FeSO_4 + O_3 = 2Fe_2(SO_4)_3 + Fe_2O_3$$

the leaching operation:

$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$$

and the precipitation:

$$CuSO_4 + Fe = Cu + FeSO_4$$

[1] U. S. Patent 814,836, March, 1906.

so that the leaching solution, is therefore regenerated by the precipitation of the copper with iron. The ferrous sulphate solution is then again applied to the ore, and while hot, air is passed through it, thereby regenerating the ferric sulphate, which attacks the copper and makes it soluble, thus repeating the cycle. It is claimed that the process is applicable to ores containing too much lime for acid treatment.

The Laist Process.—This process is based on the use of sulphuric acid as the solvent, and hydrogen sulphide as the precipitant.

The steps in the process may be summarized as follows:

1. Dissolving copper from the ore with dilute sulphuric acid.
2. Precipitating the copper from its solution as copper sulphide by hydrogen sulphide, accompanied by the regeneration of acid.
3. Manufacture of the hydrogen sulphide gas: *a*. Reduction of gypsum to calcium sulphide with coal; *b*. Decomposition of the calcium sulphide by carbon dioxide and water to hydrogen sulphide and calcium carbonate.
4. Conversion of the copper precipitate to metallic copper.

The process is based on the following reactions:

(1) $CuCO_3 + H_2SO_4 = CuSO_4 + CO_2 + H_2O$.
(2) $CuSO_4 + H_2S = H_2SO_4 + CuS$.
(3) $CaSO_4 + 4C = CaS + 4CO$.
(4) $CaS + H_2O + CO_2 = CaCO_3 + H_2S$.

The first well-known reaction shows what takes place when copper carbonate or oxide is dissolved with sulphuric acid. Reaction 2 shows the effect of the hydrogen sulphide on the copper sulphate, by which the copper is precipitated as sulphide and an equivalent amount of sulphuric acid regenerated. The third reaction, is the first step in making the hydrogen sulphide gas. Calcium sulphate (gypsum) is reduced with coal. This reaction takes place at a bright red heat, or about 1800° F. The reaction is accompanied by the formation of both carbon dioxide and carbon monoxide, but the monoxide largely predominates. In the reaction it is assumed that carbon monoxide only is formed. From the fourth reaction it is seen that when calcium sulphide is treated with water and carbon dioxide, it decomposes, and calcium carbonate and hydrogen sulphide are formed.

From the reactions it is clear that 168 parts of gysum will furnish enough hydrogen sulphide to precipitate 63 parts of copper. For the reduction of this gypsum 48 parts of carbon is required. In practice there is used 3 parts of coal to 7 parts of anhydrous calcium sulphate, that is to about 8 parts of gypsum. This slight excess of coal is necessary to effect a quantitative reduction. Hence about 4 lb. of the mixture of coal and gypsum are used in precipitating 1 lb. of copper, or about 2 2/3 lb. of gypsum, or 1 1/4 lb. of calcium sulphide precipitate 1 lb. of copper.

The copper sulphide precipitate is readily converted into metallic copper, while sulphur dioxide is released.

Most copper ores contain substances besides copper which consume acid. Acid lost in this way is not recovered in the precipitating tanks, but is recovered by allowing the acid solution itself to flow down condensers up which sulphur dioxide mixed with air from the copper sulphide furnace, is passed. The hot air in conjunction with iron salts in the solution oxidize a large part of the sulphurous acid to sulphuric acid.

Method of Extracting Copper at Rio Tinto, Spain.[1]—The ore treated at Rio Tinto is massive iron pyrite containing up to 3 per cent. of copper, which has been disseminated through the mass by a secondary enrichment.

The well-known method adopted for the extraction of the copper, and in use at the present time, consists in allowing huge heaps of the mineral to oxidize under the influence of moisture and air, and subsequently washing out the copper sulphate as soon as it is formed, by running water through the heap.

The application of this system depends largely on the state in which the copper occurs in the mineral. If it exists as chalcopyrite—$CuFeS_2$—the copper will not oxidize by simple exposure to the air, in one case it having taken many years to oxidize 10 per cent. of the copper originally present in the ore. If the copper is in the form of CuS, the oxidation proceeds very slowly. The best form for solution is Cu_2S, or copper glance, which constitutes the bulk of the copper in Rio Tinto pyrite. These statements may be made clearer from the following account of the reactions that take place during the oxidation.

When the mineral is exposed to free access of air and moisture, some ferrous sulphate is formed in accordance with the following reaction:

$$(1)\quad FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4$$

This ferrous sulphate becomes readily oxidized by the air to ferric sulphate,

$$(2)\quad 2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O,$$

and it is due to the reaction of this ferric sulphate on the copper sulphides that the copper is rendered soluble, as is shown by the following chemical equations:

$$(3)\quad Fe_2(SO_4)_3 + Cu_2S = CuSO_4 + 2FeSO_4 + CuS.$$
$$(4)\quad Fe_2(SO_4)_3 + CuS + O_3 + H_2O = CuSO_4 + 2FeSO_4 + H_2SO_4$$

The reaction No. 3 takes place fairly rapidly and causes half the copper to go into solution within a few months, while reaction No. 4 proceeds

[1] C. H. Jones, Trans. Am. Inst. Min. Engs., Vol. XXXV, 1905.

much more slowly, and requires, under the most favorable conditions, about two years to extract 80 per cent. of the remaining half of the copper.

In the laboratory at Rio Tinto a method has been worked out to determine the state of combination of the copper in any particular mineral. This method depends on the action of the mineral on various solutions under constant conditions of dilution and temperature, and, though necessarily somewhat arbitrary, it shows with considerable accuracy the form of the sulphide in which the copper exists, and consequently whether the copper can be readily extracted by washing in heaps.

In practice the method adopted to bring about the desired oxidation is as follows: A site is chosen for the formation of the heap where the ground is sufficiently concave and sloping to enable the copper liquor that is formed to collect and run out at the base of the heap. On the ground is first arranged a net work of air flues, made of rough stones and having an internal diameter of 12 in. Vertical chimneys, 50 ft. distant from one another, are built in the same manner and connect with the ground flues. Care is taken that the mouths of the ground flues are kept open and not covered by ore. The mineral, the lump portion of which has been passed through jaw breakers to be reduced to pieces not larger than from 2 to 3 in. across, is now tipped from side-tip wagons at the highest part of the selected side over and around the stone flues. Lump and fines are alternately dumped until the height of the mass at the edge is about 30 ft., the upper surface of the mineral being kept level. A heap of this form approximately contains 100,000 tons of ore.

As the mineral is added, the building of the stone chimneys keeps pace, in order to have a clear opening to the top of the heap. The surface of the heap is formed into squares by means of ridges of the mineral, the size of these squares depending on the porosity of the heap. The function of these ridges is to enable the water to be run on locally over the surface of the heap in order to insure that all parts are equally washed and that the water does not run through the heaps in channels. A system of gutters is also arranged so that the water can be run on to all parts of the mass. As the heap is being formed, water is run on and the copper sulphate existing in the mineral is extracted; also, the water provides the moisture for the oxidation to take place in accordance with the equations given above. The mineral in the heap is then allowed to oxidize, which it does pretty rapidly, as evidenced by the heat produced, the temperature in the chimneys rising to from 170 to 180° F. As the temperature increases, the surface openings of the chimney may be closed in order to allow the oxidation to spread through the heap. The surface gradually shows a brownish coloration, due to the dehydration of the buff-colored basic ferric salt that forms on top of the mass, and its

gradual heating up may be noted by this drying action. The greatest care must be taken not to allow the heaps to fire, for if once started it is very difficult to extinguish. When the oxidation has proceeded as far as it is safe to allow it, water is run on at the rate of about 50 cubic meters per hour, until the soluble copper is leached out. The heap is then allowed to reoxidize and the washing is repeated. After about a year has elapsed the surface requires "retilling," and the squares are rearranged so that the places where the ridges were before are now the middle of the squares. The gutters also are shifted. At the edge of the heap for a distance of some yards the mineral, which has become cemented, holds a considerable quantity of copper salts and is dug down into terraces in order that this copper may be extracted by washing.

When the copper is reduced to 0.3 per cent. the heap is considered washed and the mineral, containing 49.5 per cent. of sulphur, is removed and exported as "washed sulphur ore" and used for the manufacture of sulphuric acid.

Successful heap washing depends on the efficient ventilation of the mass, the trouble usually being a too great excess of fines produced in mining the ore, which cement hard and clog up the air passages.

The copper liquor as it runs from the heap contains some ferric iron in solution, which as will be shown later, is very objectionable. In order to remove the ferric iron the liquor is run over a smaller heap of fresh mineral known as a "filter bed," which reduces the ferric iron. This "bed" is laid inside a reservoir formed by a masonry dam across a small ravine, and the liquor after percolating through the mineral remains in contact with it until it is required to be drawn off to the precipitating tanks. When the mineral is fresh the reduction of the ferric iron takes place rapidly, due to the Cu_2S, as shown by equation 3, but the iron pyrite itself has an effective reducing action on ferric iron in solution according to the following equation:

$$(5)\quad 7Fe_2(SO_4)_3 + FeS_2 + 8H_2O = 15FeSO_4 + 8H_2SO_4.$$

The principal constituents of the liquor as it enters the cementation tanks are as follows, the figures given representing the grams per cubic meter or units per million parts: Copper 4000, ferric iron 1000, ferrous iron 20,000, free sulphuric acid 10,000, and arsenic 300. The large quantities of ferrous iron and free sulphuric acid present are due to the fact that the waste liquor from the cementation tanks after the copper has been precipitated, is pumped back and used for washing the heaps in addition to fresh water, and consequently these solutions tend to become concentrated. The liquor is then run from the reservoirs at about 300 cubic meters per hour through the precipitation tanks over pig iron in order to precipitate the copper in the form of "cement copper." These cementation tanks are arranged in series on the slope of a hill, the liquor

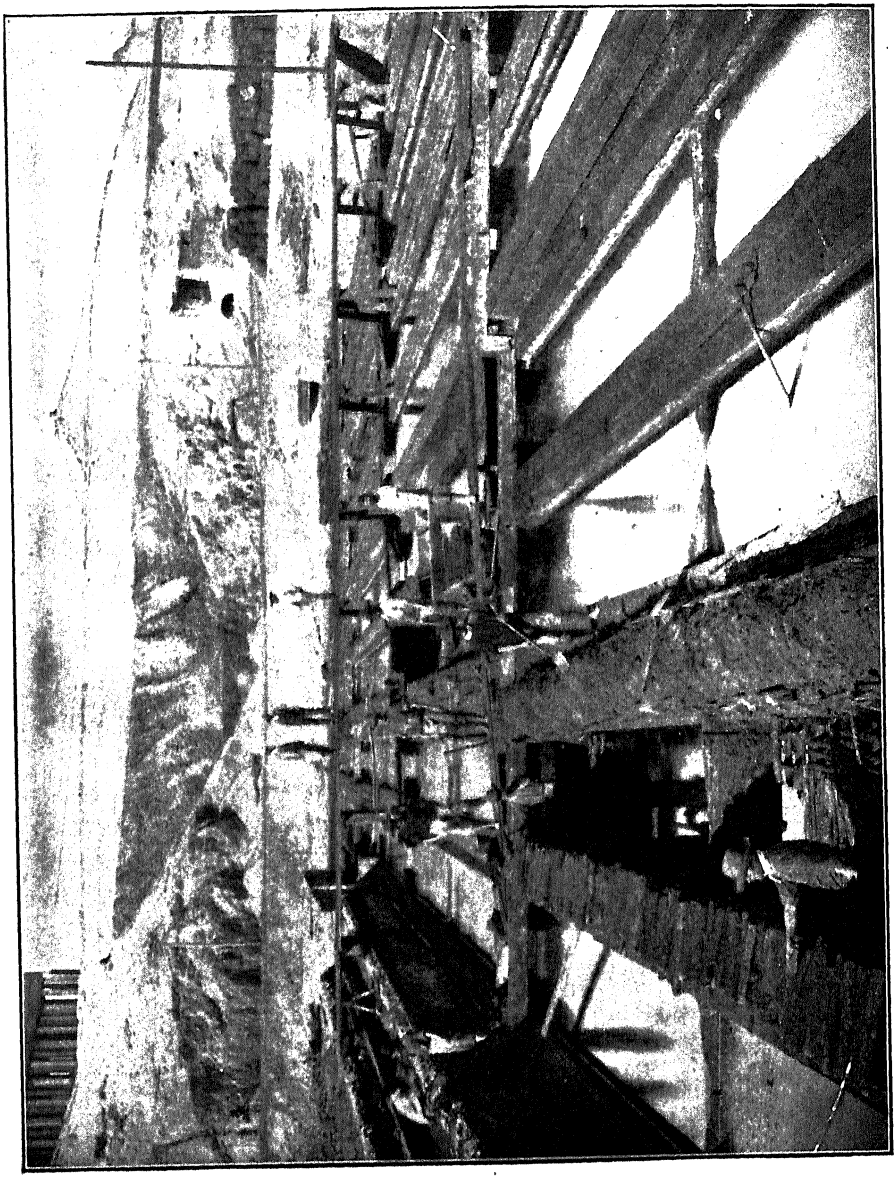


FIG. 46.—Rio Tinto leaching plant, Spain. View showing copper precipitators.

passing backward and forward until it is discharged from the lowest tank of the series free from copper.

Each series consists of three tanks in parallel arranged so that the liquor can be divided and passed along as many tanks as necessary, depending on the quantity of liquor that is being run through and on the varying temperature of the liquor with different seasons, the hotter the solution, which in summer reaches 100° F., the faster the rate of precipitation. Each tank is about 320 ft. long, 5.5 ft. wide by 2.25 ft. deep, and has a slope varying from 2 per 1000 in the first series to 11 per 1000 in the last, the reason for the increase in slope being, that as the liquor becomes impoverished in copper the free acid present is more active in wastefully dissolving the pig iron—an action which is considerably

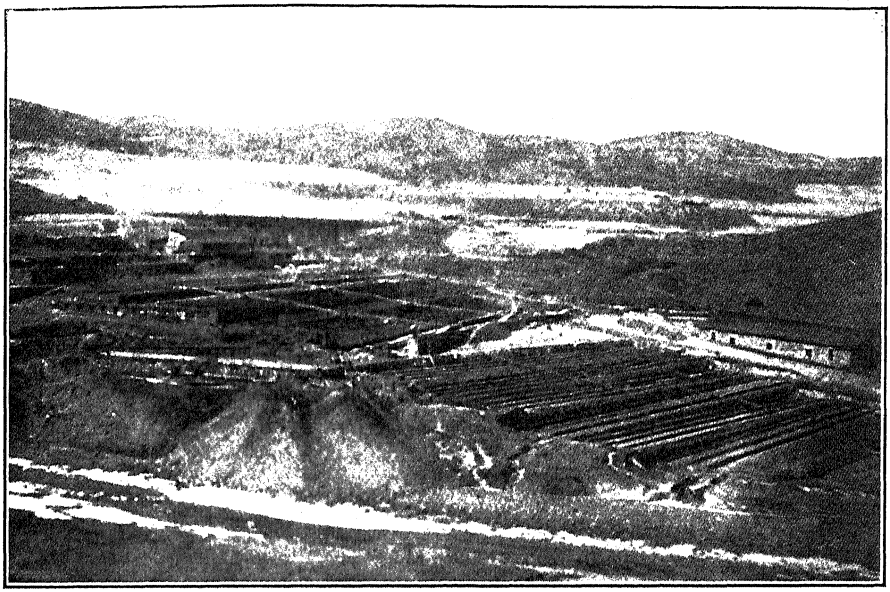


FIG. 47.—Rio Tinto leaching plant, Spain. General view of mineral heaps, copper liquor dam, and precipitating tanks.

diminished by increasing the velocity of the liquor by means of the increased slope of the tanks. The tanks themselves are made of 9×3 in. boards attached to wooden frames set in cement, the space between parallel tanks being filled with stone and cement, constituting a wall supporting the sides of the tanks. Fig. 46 shows the method of removing the cement copper and Fig. 47 a general view of the mineral heaps, copper liquor dam and precipitating tanks.

No metal is used in the tank construction, hard wood pegs being employed to attach the boards to the frames. The spaces between the boards

are carefully caulked with oakum and pitch in order to render the tank water-tight. At each end of the tank is an arrangement by which a door can be dropped in and luted so as to cut out that particular tank, and there are also wooden plugs that can be removed so that the liquor from that tank can be run off, thus allowing for the removal of the precipitated copper. A few old boards are placed on the bottom of the tanks for their protection and on these are piled up the pigs of iron which are laid across the tank at the bottom, the next layer being at right angles to the first, and so on until the tank is filled; each foot-length of the tank contains about one ton of iron. The liquor is allowed to run through the system of tanks and needs no attention except to remove the precipitated copper and to add fresh iron. The "salida" liquor containing from 15 to 20 grm. of copper per cubic meter is allowed to run to waste, for the reason that about this copper content the amount of iron required to precipitate the copper equals the value of the copper recovered. Daily some of the tanks are cleaned out by being closed as described above, the liquor meanwhile passing down the other tanks of the series; the liquor is run off into settling tanks, any copper in suspension being recovered; all of the iron is removed from the tank and piled on to the dividing wall, at the same time the copper adhering to the iron is knocked off and thrown back into the tank. The dirty-looking precipitate is then transferred to the cleaning and concentrating plant, the iron is replaced in the tank and the liquor again allowed to run through it. This crude precipitate, containing about 70 per cent. copper, is thrown, a little at a time, on a perforated copper plate at the head of a long launder or tank and is washed through the plate by a strong stream of water from a small nozzle. The material that does not pass through the screen consists of leaf-copper and small pieces of iron; this material is thrown into a heap and afterward sorted over by girls who remove the pieces of iron. The precipitate that passes into the launder is repeatedly turned over against the stream of water and by this simple means a concentration is effected.

The first few yards of the launder contain a red precipitate known as "No. 1 precipitate", containing 94 per cent. copper and less than 0.3 per cent. arsenic; following this is "No. 2 precipitate" containing 92 per cent. copper and between 0.3 per cent. and 0.75 per cent. arsenic, while below is the "No. 3 precipitate"; this is in a state of very fine division and contains on an average 50 per cent. copper and 5 per cent. arsenic. This last named portion, which carries all the graphite from the pig iron, contains the bulk of the antimony and bismuth that is also precipitated from the liquors. Classes No. 1 and No. 2 are removed to the drying sheds and bagged for shipment to the refinery; the No. 3 precipitate is removed, moistened with acid liquors, made into balls by hand and dried in the sun. These balls become cemented hard and can be readily transferred to the smelter, where they form part of the charge for the

blast furnaces and are run down to matte to be subsequently bessemerized, thus effectively removing the arsenic, antimony, and bismuth they contain. The reactions that take place in the cementation tanks are given in equations 5, 6, and 7.

The first reaction that occurs in the liquor running over metallic iron is the reduction of the ferric sulphate to ferrous sulphate, the final result being in accordance with the equation:

$$(5)\quad Fe_2(SO_4)_3 + Fe = 3FeSO_4.$$

This action causes the consumption of the pig iron without any corresponding yield in copper, and consequently should be avoided as far as possible by having all the iron in the ferrous condition. The second reaction is the precipitation of the metallic copper, brought about by galvanic action. The iron becomes coated with copper, and thus the iron and copper in the acid liquor constitute a galvanic couple with a considerable difference of potential. It is due to the electrolytic action that the copper and all other metals present that are electro-negative to iron will be precipitated. The ultimate action of the precipitation may be chemically expressed by the following equation:

$$(6)\quad CuSO_4 + Fe = FeSO_4 + Cu.$$

Besides the reactions above mentioned there is one which causes the liberation of hydrogen, as evidenced by the bubbles of gas that may be observed to arise in the tank liquor. This action, which causes a wasteful consumption of iron, may be expressed as a final result by the following equation:

$$(7)\quad Fe + H_2SO_4 = FeSO_4 + 2H.$$

These three equations constitute the main reactions that take place in the precipitating tanks.

While the liquor is fairly strong in copper, the copper is mostly precipitated in a coherent form, but in the later stages, as the liquor becomes impoverished it is precipitated in a powdery state—a condition which is more effective in its galvanic action with the iron, and thus unfortunately causes a larger precipitation of arsenic and other impurities than in the earlier stages. In the later stages also the "solution reaction," of iron and sulphuric acid as given in equation No. 7 goes on to a proportionately greater extent than does the precipitation of the copper, and consequently the cost of pig iron in precipitating the copper varies inversely as the quantity of copper in the liquor.

By keeping careful watch on the reduction, as far as possible, of the ferric iron before the liquor enters the tanks, and by giving it sufficient velocity through the tanks, a strongly acid liquor such as given above during a years' working will not consume more than 1.4 units of pig iron

(containing 92 per cent. iron) to 1 unit of copper precipitated. A valuable check on the iron being consumed can easily be kept by the laboratory, by analyzing the liquors before entering and after leaving the tanks, and from these analyses the quantity of iron that is being consumed can be calculated.

The following table[1] gives the analysis (in grams per cubic meter) of the entering and outgoing liquors of the precipitation plant at Rio Tinto:

	Entering	Leaving	Entering	Leaving
Copper	2,710	19	2,780	19
Ferrous iron	13,908	17,202	14,030	17,934
Ferric iron	610		732	
Free acid	4,874	4,129	4,991	4,349
Total solids	70,872	69,662	71,980	72,834
Specific gravity	105.818	105.718	105.901	105.972
Consumed iron	1.26 to 1 Cu		1.26 to 1 Cu	

The best results are obtained when the solution is slightly acid, as it tends to accelerate precipitation and prevents a falling out of basic salts of iron while the precipitation is going on.

At Tharsis the inclination of the precipitating tanks is as follows:

For the first 40 per cent. of the copper,	1 in 200
For the next 30 per cent. of the copper,	1 in 150
For the next 20 per cent. of the copper,	1 in 100
For the remainder,	1 in 50

At Rio Tinto and Tharsis, 1.4 units of pig iron containing 92 per cent. iron are consumed on an average, per unit of copper obtained. Both at Rio Tinto and Tharsis the liquor traverses about 3 kilometers before all the copper is precipitated. Sixty per cent. of the copper in the liquors is precipitated within the first 700 meters of the tanks. Over 70 per cent. of the precipitate contains more than 94 per cent. copper.

The following points have been established by the practice at Rio Tinto:

1. The complete analysis of the solutions both before and after treatment is essential to prevent undue consumption of iron.

2. Free acid to be eliminated as much as possible.

3. Mechanical contrivances will, in a measure, overcome these difficulties. The inclination of precipitating tanks and consequent velocity of current should be in inverse ratio to the amount of copper present; the less the copper and the greater the free acid and ferric iron, the greater inclination necessary.

[1] F. H. Probert, *Mining and Scientific Press*, January 4, 1908.

4. As large a surface of iron should be exposed to the liquors as possible.

5. Aeration of the liquor by tumbling through the air is objectionable, since it has an oxidizing effect and so increases the consumption of iron.

6. In the course of the flow of the liquor through the precipitating tanks there is a place where the cost of iron exceeds that of the value of the copper obtained.

7. The warmer the liquors, within certain limits, the faster is the precipitation of the copper.

M. P. Truchot, chief chemist, Huelva,[1] estimates that to extract copper by natural weathering alone, 20 years would be necessary; roasting destroys the vegetation of the country; there therefore remains the wet methods where the reactions may be hastened by the use of a regulated supply of air and water. In preparing the heaps for oxidizing leaching of the copper, the fines amount to 80 per cent.; the lumps, 20 per cent. The two grades are placed in alternate layers and the top of the heap finished with fines, to prevent too rapid filtration. Practice varies as to the temperature of the heap, which may be as high as 82 to 90° C. where it is sought to promote oxidation and to increase the rate of leaching, while in other cases, the temperature is not allowed to exceed 30 to 32° C. Since the higher temperature is dangerous, one of no more than 45 to 60° C. is recommended.

It takes 6 to 7 years to exhaust one of these heaps of 100,000 tons; the exhausted ore then contains 0.25 to 0.30 per cent. of copper. The more permeable copper schists leach more rapidly, however, taking but three or four years. While the oxidation of chalcopyrite proceeds but slowly, the rate can be increased by finely pulverizing it and distributing it throughout the pile.

The copper solution from the heaps varies from 0.015 to 0.5 or even 0.6 per cent. Cu. It is of a reddish-green color containing ferric and ferrous sulphates, free sulphuric acid, copper sulphate, and other salts.

When the water supply is abundant, and the free acid is consequently low, the consumption of pig iron varies from 1.3 to 1.5 tons per ton of copper precipitated. This seldom occurs, however, and generally there is needed 1.75 to 2 tons per ton of copper extracted; that is more than double the theoretical quantity.

Treatment by Heap Roasting and Leaching.—Instead of extracting or treating all the material by weathering, the extraction of the copper may be expedited by first giving the heaps a slow roast, by which process much of the copper in the cupriferous pyrites is converted into sulphate and can readily be leached. The production of sulphate of copper by slow heap roasting can only be used on ores that contain proportionately large amounts of iron pyrites and small amounts of copper pyrites or

[1] L' Echo des Mines et de la Metallurgie, 1906, p. 482.

other copper sulphides. In the slow and imperfect roasting in heaps or stalls not all of the copper sulphide will be converted into sulphate; a part will always remain unaffected, and another part will be transformed into oxides. In order to extract as much copper as possible from the ores, after the roasting has been finished and the sulphate of copper leached out, the ores are allowed to weather, as for the fresh or unroasted ores, already described, whereby in the course of time the copper is converted into sulphate, by natural weathering.

The production of sulphate of copper by roasting, followed by weathering of the leached roasted ore, was used for a long time at Rio Tinto, in Spain. According to Schnabel,[1] the ores thus treated were cupriferous pyrites with 1 1/2 to 2 percent. copper; these were slowly roasted in heaps of 200 to 1500 tons upon a bed of brushwood, firewood or coals. The 200 ton heaps were hemispherical, 26 ft. in diameter at the base and 11 ft. 6 in. high. The larger, 1500 ton heaps were elliptical in plan, the longer axis of the ellipse being 55 ft. 9 in., and the shorter axis 32 ft. 10 in.; their height was also 11 ft. 6 in. Air was admitted by means of a system of channels traversing the heaps. The smaller heaps burned for two months, the larger ones for six. To roast 100 tons of ore required in the small heaps 27 cu. ft. of wood and in the larger ones 9 cu. ft. The yield of copper was greater in the small heaps than in the larger ones. The roasted ores were leached for 50 hours by which means the copper present as sulphate was washed out of them. The exhausted residues still contained 0.4 to 0.5 per cent. of copper, chiefly as sulphide, to extract which the ores were allowed to weather. With this object they were piled on a system of horizontal flues built of dry stone, that air could circulate through the pile of ore. The vertical flues were continued in proportion as the heaps got higher by the piling on of additional ore. As soon as the damp heap had reached a certain height, the sulphides began to decompose, as was shown by the rising temperature. By checking the air supply it was kept, if possible, from rising so high that the heap took fire. From time to time, the heap, or a portion of it, if it was a large one, was leached out, and the liquor conducted to the precipitating tanks. The exhaustion of the heaps, which were continually being increased, and which may reach 500,000 tons, will not be completed in measurable time, as, in spite of frequent leaching, the weathering proceeds very slowly. It is even held that these huge heaps will still be producing sulphate of copper long after the mines shall have been worked out.

The cost of producing copper at Rio Tinto, Spain, by heap roasting and leaching, is stated to be about $1.55 per ton, divided as follows: Mining 89 cents, roasting about 18 cents, including labor in building heaps, etc., precipitating and collecting about 56.6 cents. Sixty-six tons of ore were required to produce one ton of metallic copper.

[1] Handbook of Metallurgy, Vol. I, p. 212.

The cost of producing one ton of metallic copper by the cementation process as carried out there is about $144.00.

The first cement copper was produced in Spain at Rio Tinto, in 1752 from heaps of low-grade sulphide ore that had undergone decomposition through natural processes. The copper was leached out by water, the metal being precipitated on iron. It was first thought to be merely a coating of copper on the iron, but it was found if left long enough, the replacement became complete.

ELIMINATION OF ARSENIC, ANTIMONY, AND BISMUTH.

Atmospheric Oxidation, Without Burning.[1]—In atmospheric oxidation of cupriferous pyrites, and subsequent extraction of copper by leaching, as carried on in Portugal and Spain, arsenic and antimony are to some extent dissolved and precipitated with the copper. The proportion in which they are separated and precipitated is only a fraction of the amount contained in the ores, as shown by the following tables by Allen Gibb:

	Pyrites		Precipitate		Total per cent. of elimination
	Per cent. actual	Per cent. relative Cu = 100 per cent.	Per cent. actual	Per cent. relative Cu = 100 per cent.	
Copper.....	2.00	100.0	62.0	100.0	
Arsenic.....	0.40	20.0	3.5	5 64	71.8
Antimony.....	0.03	1.5	0.08	0.129	91.4
Bismuth.....	0.016	0.8	0.06	0.097	87.9

Burning and Subsequent Washing.—In this process largely used in Spain and to some extent in Portugal, for the extraction of copper from cupriferous iron pyrites, there is a considerable elimination of arsenic, antimony, and bismuth in burning. The following table, by Gibb, may be taken as fairly typical of heap roasting, preparatory to leaching, as conducted in Spain.

	Raw Pyrites		Burnt Pyrites		Total per cent. of elimination
	Per cent. actual	Per cent. relative Cu = 100 per cent.	Per cent. actual	Per cent. relative Cu = 100 per cent.	
Copper.....	2.45	100.0	3.32	100.0	
Arsenic.....	0.43	17.55	0.133	4.08	76.8
Antimony....	0.029	1.18	0.030	0.92	22.0
Bismuth.....	0.015	0.61	0.017	0.52	14.8

[1] Allen Gibb, Trans. A. I. M. E., Vol. XXXIII, p. 667.

CHLORIDE PROCESSES

The chloride processes have been widely applied to the extraction of copper from its various ores. Hydrochloric acid, ferric and ferrous chlorides, are the solvents usually employed.

Hydrochloric acid presents certain advantages over sulphuric acid in the technical operation, but is usually more expensive, especially in copper mining districts. Sulphuric acid, in the process of operation, forms ferric sulphate, which when exposed to the air is decomposed into basic sulphate of iron and free sulphuric acid, consequently consuming more iron in the precipitation of the copper. Hydrochloric acid is less apt to form basic salts and therefore yield solutions that contain but little free acid, and which, accordingly, require less iron for the precipitation of the copper, than do solutions containing ferric sulphate. On the other hand it attacks oxide of iron more energetically than does sulphuric acid, but the ferric or ferrous chloride so formed is more likely to be precipitated out of the solution as the insoluble ferric oxide, than from a sulphate solution.

Ordinarily only oxidized ores are applicable to treatment by a chloride process. The copper may be dissolved either by

Hydrochloric acid, or
Metal chloride.

The acid, however, is the solvent usually employed. The chlorides have been used as solvents on both oxide and sulphide ores but on sulphide ores the action has been too slow for profitable application, although both ferric and ferrous chlorides were quite extensively used at one time.

Hydrochloric Acid.—If iron is used as the precipitant, as it usually is, the hydrochloric acid process consists essentially of applying dilute hydrochloric acid to the oxidized ores of copper, which reacts with the copper oxide thus:

$$CuO + 2HCl = CuCl_2 + H_2O$$

to form cupric chloride. Some cuprous chloride may also be formed:

The cupric chloride thus formed is filtered from the ore and precipitated with iron, thus:

$$CuCl_2 + Fe = FeCl_2 + Cu$$

the iron and copper changing places. The copper is precipitated while the iron goes into solution as ferrous chloride. Theoretically the same amount of iron is required to precipitate a pound of copper from cupric chloride solutions as from cupric sulphate solutions *i.e.*, 56 lb. of iron to precipitate 63.6 lb. of copper. In practice, however, it will usually take less for chloride than for sulphate solutions. If the copper in solution is in the form of cuprous chloride, only half the amount of iron is required

as that used when the copper is in the form of either cupric chloride or cupric sulphate.

If hydrochloric acid is used as the solvent is takes theoretically approximately 0.6 lb. of acid to extract 1 lb. of copper as cuprous chloride, and 1.1 lb. as cupric chloride.

In practical operation, much more acid is required, the amount depending largely on the nature of the ore. The theoretical amount of acid given to react with the copper, is supposed to be the pure acid, free from water. Commercial hydrochloric acid, is the HCl dissolved in water, so that in estimating the commercial acid required, it will be necessary to first know the acid content, which can be determined from its specific gravity.

Concentrated HCl+Aq loses HCl, and dilute HCl+Aq loses water on warming, until an acid of constant composition is formed, containing 20.18 per cent. HCl with a specific gravity of 1.101 at 15° C., which can be distilled unchanged at 110° C. Concentrated HCl+Aq gradually gives off HCl on the air until it has a specific gravity of 1.128 at 15° C., and contains 15.2 per cent. HCl. In leaching copper ores, only very dilute solutions of hydrochloric acid are usually employed, rarely exceeding 5 per cent. HCl.

In Stadtberg, Westphalia, hydrochloric acid was formerly used to extract copper from ores containing from 1 to 2 per cent. copper.[1] The leaching vessels were rectangular tanks of wood 4 ft. 1 1/2 in. high, packed in a bed of clay 1 ft. 3 in. thick, then fitted with a grating of wooden bars, upon which the ore was piled. The first tanks held 29 tons of ore, but those erected afterward had a capacity of 90 tons. All the tanks were situated on a level. The leaching was methodical; ores nearly free from copper being treated with fresh hydrochloric acid of 12 to 13° B., as obtained from soda works, while fresh ore was treated with partially saturated solution until the latter was fully saturated, which took place at 19 to 20° B. The various solutions were allowed to remain 12 hours in each tank, the saturation point being reached in 10 to 12 days. The solution was circulated by means of pumps and bucket wheels. After the solution had percolated through the ores, it ran out through a plug hole to which the bottom of the tank was inclined, into receivers, whence it was again lifted to its proper tank. The exhausted ore was allowed to lie for another 12 to 15 hours in water and was then washed for 12 hours more. Fresh acid was diluted with a portion of the mother-liquor. For each 100 parts by weight of copper, 550 to 700 parts of hydrochloric acid 12 to 15° B., were employed. This process replaced the sulphuric acid leaching, previously employed but was later abandoned when the carbonates of the ore were replaced with sulphides in depth.

[1]Schnabel Handbook of Metallurgy, Vol. I, p. 200.

At Twiste, in Waldeck, attempts were made to leach malachite and azurite copper ores occurring in the Bunter Sandstein (Lower Trias) and containing 1/2 to 1 per cent. of copper, by means of hydrochloric acid, but had to be abandoned because the ores contained from 1/2 to 1 per cent. of lime which was dissolved by the acid before it attacked the copper.

Ferric Chloride, $FeCl_3$.—Ferric chloride, like ferric sulphate, has the property of dissolving copper from its oxide, carbonate, and sulphide combinations. If the sulphides of iron, copper, lead, zinc, arsenic and antimony are treated with a hot solution of ferric chloride, the minerals are more or less decomposed, and the respective metals go into solution as chlorides, usually with the liberation of sulphur. Hydrochloric or sulphuric acid, added to the solution, aids the reactions. Silver is converted into chloride by the action of ferric chloride. Gold remains unaffected.

If ferric chloride is used as a solvent for ore containing the copper as cupric sulphide (CuS), cupric chloride is produced and the ferric chloride is reduced to the ferrous chloride:

$$CuS + 2FeCl_3 = CuCl_2 + 2FeCl_2 + S.$$

If the copper mineral contains the copper as cuprous sulphide the reaction will result in the formation of cupric and cuprous chlorides:

$$Cu_2S + 2FeCl_3 = 2CuCl + 2FeCl_2 + S$$
$$Cu_2S + 4FeCl_3 = 2CuCl_2 + 4FeCl_2 + S.$$

With a neutral solution of ferric chloride, the reaction with copper oxide is:

$$3CuO + 2FeCl_3 = 3CuCl_2 + Fe_2O_3$$

although some cuprous chloride may also be formed by the reduction of the ferric to the ferrous chloride, and the subsequent reaction of the ferrous chloride on the copper oxide. If the solution is somewhat acid, the ferric chloride will be reduced, but the ferrous chloride will not be precipitated to any great extent. With copper carbonates the reaction is much the same as for oxides, except that carbon dioxide is liberated in the reaction.

In reacting with sulphide ores, the ferric chloride is reduced to the ferrous chloride, but the ferrous chloride does not further react with the copper sulphides. In any event, the sum total of the reactions may be considered to be the reduction of the ferric to the ferrous chloride, with the formation of cupric and cuprous chlorides.

The copper may be precipitated with iron:

$$CuCl_2 + Fe = Cu + FeCl_2,$$
$$2CuCl + Fe = 2Cu + FeCl_2,$$

ferrous chloride being formed. If ferric chloride exists in the solution during precipitation with iron, it will be reduced to ferrous chloride at the expense of the iron.

The ferrous chloride, after precipitation of the copper, may be regenerated back to ferric chloride by the action of air, chlorine, or hydrochloric acid. If the neutral ferrous chloride is regenerated by agitation with air, some of the iron is brought into the condition of basic salts, and much is precipitated as the ferric oxide.

$$6FeCl_2 + O_3 = 4FeCl_3 + Fe_2O_3.$$

From this equation it is apparent that one-third of the iron is precipitated from the solution as the insoluble ferric oxide in order to raise the remaining two-thirds to the ferric condition. In addition to the precipitated ferric oxide there may be formed, in netural solutions, insoluble oxychlorides, and these necessitate a further loss, both of iron and chlorine. If, however, iron is used as the precipitant, large amounts of ferrous chloride are produced which may then be brought to the ferric condition for reuse as a solvent, and the loss of iron as ferric oxide or oxychloride, is not a serious matter; in fact an elimination of a certain amount of the iron is an absolute necessity.

If the ferrous chloride solution is regenerated with chlorine, oxychlorides are not formed, although some iron may be precipitated as ferric oxide. The chlorine may be produced either chemically or electrolytically, by any of the well-known methods. The chlorine combines directly with the ferrous chloride to produce the ferric chloride;

$$FeCl_2 + Cl = FeCl_3.$$

The solubility of copper from sulphide ores with ferric chloride solutions, depends much on the way the copper is mineralogically combined. The copper in the form of chalcocite is much more readily soluble than in the form of chalcopyrite, while gray copper remains quite unaffected. Careful roasting at a low temperature makes the copper, in any of its sulphide combinations, readily soluble, but when roasted at a high temperature, the copper is quite insoluble either in acids or solutions of ferric salts. This is doubtless due to the formation of silicates and of ferrites.

Doetsch Process.—Ferric chloride acts on cupric and cuprous sulphides to form cupric and cuprous chlorides, while the ferric chloride is reduced to the ferrous condition. The reactions may be expressed thus:

$$CuS + 2FeCl_3 = CuCl_2 + 2FeCl_2 + S$$
$$Cu_2S + 2FeCl_3 = 2CuCl + 2FeCl_2 + S.$$

On these reactions are based the Doetsch Process, formerly used extensively at Rio Tinto in Spain. The ore there treated contained on an

average of 2.7 per cent. copper. The copper passed into solution while the pyrite was practically unaffected in the leaching operation. The process has the advantage of reducing the waste of iron in the precipitating tanks by avoiding the formation of ferric sulphate. In this way one ton of copper precipitate was obtained with an expenditure of about an equal weight of iron.

In the process as carried out at Rio Tinto the ore was crushed to about 1/2 in., mixed with 0.5 per cent. common salt and a like amount of ferrous sulphate, and built into large heaps. These heaps were from 12 to 16 ft. high and 50 ft. square at the base. A solution of ferric chloride was run in a continuous steam upon these heaps.

It took about four months to extract 1.34 per cent. of the copper, or 50 per cent. of the total copper content. After two years 2.20 per cent. was extracted or 80 per cent. of the contained copper. The final loss was about 0.48 per cent.

The solutions leached through the heaps, containing cupric and cuprous chlorides as also ferric and ferrous chlorides, were precipitated with iron:

$$CuCl_2 + Fe = Cu + FeCl_2$$
$$2CuCl + Fe = 2Cu + FeCl_2$$

ferruos chloride being formed. The ferric chloride, by its action on the ore, is changed to ferrous chloride; small amounts of ferric chloride may remain unchanged in the solution, but this reacts with the iron in the precipitating tanks and may be reduced there to the ferrous condition.

To make the process continuous, the ferrous chloride is regenerated back to ferric chloride, which is accomplished by bringing the ferrous chloride solution in contact with chlorine, in scrubbing towers.

The solution which ran from the ore heaps contained 5 to 7 kilogrm. of copper per 1000 kilogrm., or 1 cubic meter.

The chlorine gas, for the regeneration of the ferrous chloride to ferric chloride, was produced by heating salt with ferrous sulphate in a reverberatory furnace, holding 500 lb. An abundance of air was admitted through the working doors. The ferrous sulphate reacting with salt in the presence of air, produces chlorine, sodium sulphate, and ferric oxide.

$$2FeSO_4 + 4NaCl + O_3 = Fe_2O_3 + 2Na_2SO_4 + 4Cl.$$

The ferrous sulphate used is found in large quantities on the shores of the Rio Tinto river. The immense heaps of low-grade ore, "Toreros" being leached by natural cementation, also furnish salts of ferric and ferrous sulphate. During the reaction in the reverberatory furnace, some hydrochloric acid is formed; this is converted into chlorine by the action of manganese dioxide of which there was a certain amount placed near the flues of the furnace.

The gases from the furnace, consisting largely of chlorine with possibly some hydrochloric acid, were conducted to scrubbing towers, where they came in contact with the ferrous chloride solution from the precipitating tanks, and the ferrous chloride reconverted to the ferric chloride.

The Doetsch process was used both for raw and roasted ore. When roasted, the roasting was performed in heaps of truncated pyramidal form, 10 ft. high, with a base 20×26.5 ft. for those containing 800 tons, and 30×26.6 ft. for those containing 1200 tons.

At the bottom of the heaps, one transverse and three longitudinal flues, about 20 in. square, were formed by the larger blocks of mineral. Those were the firing passages, and communicated with vertical chimneys, of which there were two in the 800–ton, and three in the 1200–ton heaps. The mass of the heaps was made of lumps a little above nut size. Salt was added in the proporiton of 14 tons to 800 tons of pyrites ore. When the fire was started with a little wood, it was kept up by the heat of the burning sulphur. It was essential that no rich ore was included, as, on account of the action of kernel roasting, lumps of rich sulphide of copper were formed which could not subsequently be dissolved. Some of the roasted ore was at times mixed with the unroasted ore, for the extraction of the copper with the ferric chloride solution. The reactions between the salt and ferrous and ferric sulphates in the heaps may be expressed as follows:

$$2FeSO_4 + 4NaCl + O_3 = Fe_2O_3 + 2Na_2SO_4 + 4Cl.$$
$$Fe_2(SO_4)_3 + 6NaCl + O_3 = Fe_2O_3 + 3Na_2SO_4 + 6Cl.$$

The chlorine liberated, acting on the iron and copper sulphides, produces ferric and cupric chlorides. There are therefore present, $FeSO_4$, $Fe_2(SO_4)_3$, $CuSO_4$, $FeCl_3$, and $CuCl_2$, with an excess of salt, which changes the ferric sulphate into the ferric chloride.

An interesting modification of the Doetsch process was for some time carried out on a very extensive scale at Naya, close to Rio Tinto. In this method, the heaps, made in the ordinary way, as soon as they began to give off sulphurous fumes, were covered up with a fresh quantity of mineral, partly raw, and partly roasted, to which 2 to 3 per cent. of salt and a similar proportion of manganese dioxide has been added. The whole was formed into heaps 26 ft. high with a flat top, which was divided by gutters into squares of 25 ft. The remaining operations were effected in the usual way, the heaps being watered at intervals for months and years, the copper being slowly dissolved, and collected at the bottom of the heaps. It was necessary to break up the surface with a pick at intervals, to prevent it from becoming impermeable to water. The sulphurous acid gas in this modification of the process, in the presence of steam formed by the heat developed in the heaps, produces sulphuric acid, which acts upon the oxides in the crust of the roasted material. The

salt and manganese dioxide may, jointly with the sulphuric acid, evolve chlorine, forming ferric chloride, which decomposes the sulphides of copper and silver. It is also possible that, under the action of heat and sulphuric acid, oxygen is evolved which acts directly upon the pyrites.

The precipitation of the copper, in the Doetsch process, was effected in a series of tanks, 330 ft. long and 33 ft. wide, divided into 10 parallel series, receiving a uniform supply of copper solution. The total length was about 1300 ft. with a difference of level of 13 ft., which gave a sufficiently rapid flow. Pig iron, as run from the furnace, and scrap iron, were used; the scrap iron was put into baskets. Every 10 days the iron was removed, and after scraping to collect the deposited copper, it was returned to the tanks. The consumption of iron was a little more than one ton of pig iron per ton of copper produced.

The precipitate, as collected, was very impure, containing only 65 per cent. to 70 per cent. copper, the remainder being ferric oxide more or less arsenical, graphite from the pig iron, silica, etc. After treatment with water acidulated with sulphuric acid which dissolved the basic ferric arsenates without touching the copper, it was passed over 4/10 in. mesh sieves to separate pieces of cast iron. The precipitate passed through the sieves was washed in a current of water, where it separated, according to the order of density, into "Cascara," or copper; "Graphita," or particles of coal and graphite; and "Pucha," a fine black sand. The copper was smelted to blister copper; the graphita was smelted with rich ore, and the Pucha was made into balls, dried, and also smelted with the ore.

The cost of producing copper by the Doetsch process has been estimated by Cumenge, according to the results which he accomplished after a campaign of four months, during which he obtained 224 tons of cement copper.[1]

	Frances
Cost of leaching,	83.81
Precipitation,	181.16
General expenses,	28.04
Total per ton of cement copper,	293.01
Or per ton of pure copper,	345 francs, or $67.93

The extraction at the expiration of four months amounted to 1.34 per cent. of the 2.7 per cent. copper contents. 1.12 ton of iron was required to precipitate one ton of cement copper which is equal to 1.3 tons of iron to one ton of pure copper.

Dr. O. Froelich[2] made some experiments in dissolving copper from

[1] Notes sur le Rio Tinto by M. E. Cumenge, *Annales des mines*, Vol. XVCI.
[2] "Metallurgie," 1908, p. 206.

various sulphide ores by agitation with a hot solution of ferric chloride, the results of which are given in the following table:

Character of material	Extent of comminution	Time leached hours	Copper cont. of ore, per cent.	Copper cont. of tails, per cent.	Per cent. of extract
Chalcocite	Powder	15 1/2	0.94	0.02	99
Chalcocite	19–32 in	24	0.52	0.13	76
Chalcocite	13–32 in	66 1/2	7.6	0.51	93
Chalcocite	5–32 in	9	7.8	1.09	86
Chalcopyrite	Powder	24 1/2	7.8	small	100
Chalcopyrite	Powder	36	16.7	0.53	97
Gray copper	Powder	9	22.7	15.1	34

In these experiments the chalcopyrite was first subjected to a temperature of about 200° C. without the admission of air. The chalcocite was treated without heating.

The Froelich Process.[1]—In this process the ore is first subjected in the absence of air to a temperature between 150 and 800° C., whereby the loose sulphur is driven off. The pyrite is changed by this operation in its chemical composition and can then be chlorinated much quicker and better. As chlorinating gases, chlorine, vapor of hydrochloric acid and of ferric chloride are used. The chlorine and ferric chloride attack the sulphur compounds of copper, the hydrochloric acid and the ferric chloride attack the oxides of the copper. The proportion of the gases and vapors in the mixture are adjusted to the composition of the copper ore. Steam may also be added to the chlorinating mixture. It is preferable to make the temperature of the chlorination somewhat higher than the boiling point of the ferric chloride, about 300° C., but it can be lower if the copper in the ore occurs in combination with sulphur. In this case only chlorine gas is used. If iron is present in the ore it is chlorinated together with the copper, but more slowly, and the process is facilitated by a higher temperature. In order to regain the chlorine combined with the iron, the ore is heated to about 300° C. or more after chlorination, and a certain quantity of air is introduced during this operation.

The ferric chloride is then evaporated, and by the air separated into oxide of iron and chlorine gas, both of which are collected. The chloride of copper is not changed by this operation. Then the ore is treated with hot water, and the chloride of copper and, perhaps, a residue of ferric chloride are extracted. The solution is then introduced into a revolving apparatus containing pieces of iron, and the metallic copper is deposited in the form of cement copper. The solution now contains mainly ferrous chloride, and in order to regain the chlorine from it the

[1] U. S. Patent, 846,657, March 12, 1907.

solution is oxidized in a rotating drum to ferric chloride by means of an air blast. Then the water, and the water of crystallization are driven off by heating, and by increasing the temperature over the boiling point of ferric chloride and introducing a certain quantity of air, chlorine gas and ferrous chloride are obtained.

W. L. Austin[1] suggests the following method for treating with ferric chloride pyritic copper ores, containing the copper largely as chalcocite. The results obtained in the laboratory have been very satisfactory. The novel features introduced are (1) causing the lixiviant to rise through the ore and removing in an apparatus placed outside of the leaching vat any slimes which may be carried over; (2) causing the lixiviant to circulate rapidly through the material treated without employing moving parts within the leaching vat; (3) regeneration of the lixiviant by treating it with chlorine gas produced by the electrolysis of common salt in an apparatus specially provided for that purpose; and (4) cementation with the aid of the coke-iron couple. These features make it possible to have each succeeding stage in the process under direct supervision, and avoids complications caused by attempting to carry out two distinct operations concurrently in the same apparatus. It also avoids the use of moving parts submerged in a gritty and corrosive material.

On the basis of a plant treating 100 tons of ore in 24 hours, and assuming a 2 per cent. ore (40 lb. copper to the ton), chlorine at $0.02 per pound, and a 90 per cent. extraction, the following estimated cost of producing one pound of refined copper by this method is derived:

	Cost per lb. copper
Milling operations, comminution of the ore to ten-mesh, charging and discharging the tanks, elevating liquors, etc., total $0.50 per ton of ore treated,	$0.014
Chlorine, at $0.02 per lb.,	0.015
Iron, at $30.02 per ton for pig delivered at works,	0.015
Melting the precipitate into bars, at $8.00 per ton of precipitate,	0.005
Freight, refining charges, and selling expenses,	0.014
Repairs and renewals, office expenses, etc.,	0.013
	$0.076
Mining operations—open pit work, at $0.50 per ton of ore,	0.014
Total operating expenses,	$0.090

In this estimate no item has been inserted representing interest on cost of plant, nor amortization; on the other hand, no allowance is made for precious metals recovered, nor for possible commercially valuable

[1] Mines and Methods, January 1911.

bi-products. The figures given for costs of reagents consumed are liberal estimates.

Ferrous Chloride Process.—The action of ferrous chloride on copper carbonate was demonstrated by experiments of Schaffner and Unger in 1862. Some years later Hunt and Douglas based a process on the action of ferrous chloride on copper oxide and carbonate, which was for some time working on a commercial scale at Ore Knob, North Carolina, and at Phoenixville, Pa.

Cupric oxide and cupric carbonate are acted upon by solutions of ferrous chloride, forming cupric and cuprous chlorides and oxide of iron, and in the case of carbonates, there is also set free carbon dioxide, according to the following equations:

$$3CuO + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3.$$
$$3CuCO_3 + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3 + 3CO_2.$$

The ferric oxide is precipitated, while the chlorides of copper go into solution. Cuprous chloride, being insoluble in water, is dissolved by excess of other metal chlorides.

If the ore to be treated is a sulphide, or a matte, the copper must first be converted into the oxide by roasting. Roasting is unnecessary with oxidized ores.

The ferrous chloride used in the process, may be produced from common salt and ferrous sulphate, which by double decomposition forms ferrous chloride and sodium sulphate. After the solution was separated from the sodium sulphate, which crystallized out, if was ready for use.

When copper is precipitated from a cuprous chloride solution by iron, ferrous chloride is formed; when both cupric and cuprous chlorides are present, ferric chloride is first formed,

$$2CuCl_2 + 2CuCl + 2Fe = 2FeCl_3 + 4Cu.$$

Ferric chloride, however, reacts with iron to produce ferrous chloride

$$2FeCl_3 + Fe = 3FeCl_2.$$

The silver in the ore is converted into chloride of silver by the cupric chloride, and is dissolved in the excess of other metal chlorides.

As some of the copper is in the cuprous condition, relatively less iron is required to precipitate the copper, than is required in precipitating from a sulphate solution. The objections to the process was the formation of basic salts, and the difficulty of separating the solution from the residue, on account of the precipitated oxide of iron, which clogged the filters. Heat is not necessary in dissolving the copper, but it hastens the process, and makes the extraction more thorough.

The silver, in solution as silver chloride, may be precipitated with the copper, or separately if desired, by metallic copper. The precipitation of the silver by metallic copper in the presence of chlorides re-

quires that the whole of the dissolved copper should be in the cuprous condition. The clear solution containing the cupric and cuprous chlorides and the silver chloride may be treated with sulphur dioxide to convert the cupric chloride into the cuprous chloride, and with liberation of free acid. From such an acid solution any silver present is readily and completely precipitated by metallic copper, after which the whole of the dissolved copper may be precipitated with metallic iron, care being taken to arrest the process before the free acid begins to act on the iron. In this way a solution is obtained containing, besides the regenerated ferrous chloride, a considerable amount of free acid.

When copper ores containing lime are being treated, there is the difficulty to contend with that the ferrous chloride and calcium carbonate, in the presence of air, are decomposed into calcium chloride and ferric hydroxide.

According to Hunt[1] the hydrous silicate of copper (chrysocolla) is, like carbonate of copper, completely decomposed by a hot solution of ferrous chloride with common salt.

The Ferrous Chloride Process as Carried out at Ore Knob, Ashe Co., N. C.[2]—At Ore Knob, in North Carolina, the ore was crushed to 40 mesh and roasted. The average composition of the crude ore, as taken from the two shafts, was as follows:

	No. 1	No. 2
Chalcopyrite,	11.33 per cent.	13.30 per cent.
Pyrhotite,	37.46	35.74
Ferric oxide,	8.14	16.34
Alumina,	1.84	1.49
Manganese,	0.16	0.50
Lime,	5.32	7.84
Magnesia,	0.35	0.94
Carbonic acid,	4.76	7.19
Zinc,	0.67	0.66
Cobalt,	0.09	0.09
Nickel,	0.71	0.92
Silicious residue,	29.10	13.57
	99.93	98.58
Metallic copper,	3.92	4.60

This ore was sorted to bring the average copper content up to about 12.0 per cent. The average composition of the copper in the roasted ore is represented by the following analysis:

Copper as sulphate,	3.76 per cent.
Copper as oxide,	7.75 per cent.
Copper as sulphide,	0.39 per cent.
	11.90 per cent.

[1] Trans. A. I. M. E., Vol. X, p. 12.
[2] T. A. I. M. E., Vol. II, p. 394, E. E. Olcott.

The roasted ore was conveyed to agitating tanks, which were eight in number, 8 ft. in diameter, and 5 ft. deep, with raised conical bottoms. These tanks were each charged, once in 24 hours, with 3000 lb. of roasted ore and 1500 gallons of the solution of ferrous sulphate and common salt, making about 22° B., and heated by steam to 160° F. This mixture was kept in agitation for eight hours by means of suspended stirrers, consisting of a vertical shaft with a horizontal blade at the lower extremity, while at the top was attached a bevel gear which gave to the stirrers a speed of 25 revolutions per minute. After eight hours the stirrers were stopped, and the contents of the tank allowed to settle for four hours, when the clear liquor was drawn off into the precipitating tanks, and the remaining portion holding in suspension ferric oxide and particles of gangue, was drawn into settling tanks. The sands, remaining, were then washed, first with hot strong solution, and then with weaker solution. These washing liquors were allowed to settle in the settling tanks, when the clear portion was drawn off into precipitating tanks containing iron. The wet sands were then removed from the agitators to leaching tanks where a portion of the adhering solution, containing copper, was recovered.

The slimes were allowed to accumulate in the settling tanks till they were about half full, when they were washed with solution and water till they contained about 1/2 of 1 per cent. of copper. They were then washed. The settling tanks were 20 in number, 10 ft. in diameter and 5 ft. deep.

The strong liquors from the agitators were capable of holding 50 lb. of copper in solution per 100 gallons, but weaker solutions were desired as they lessened the risk of the deposition of cuprous chloride by cooling. 30 lb. of copper per 100 gallons was found a convenient strength.

The hot and strongly colored liquors were run through launders into the precipitating tanks. These were 12 in number, 12 ft. in diameter and 5 ft. deep, containing each, 12,000 lb. of scrap iron. The temperature of the precipitating tanks was maintained at 160° F. by the injection of steam. From 12 to 18 hours sufficed to precipitate all but a trace of the copper from the liquors, which were then drawn off into a lower tank and from there pumped into the stock tanks to be again used on a fresh portion of the ore.

For the precipitation of the copper wrought iron was used. The copper was removed from the precipitating tanks when they contained from 4 to 5 tons each. The consumption of iron was 70 per cent. of the pure copper produced. The cement copper, after being washed and dried, contained generally from 75 to 85 per cent. copper. The impurities were chiefly ferric oxide and earthy gangue matter.

The cement copper produced at Ore Knob costs a little less than 8 cents per pound of copper, including all expenses for mining, treating

and packing. Of this sum nearly two cents was for metallic iron. These costs were based on a production of 400,000 pounds of copper.

Hunt and Douglas Process.[1]—In the Hunt and Douglas process the copper is dissolved as sulphate and precipitated as the insoluble cuprous chloride. The cuprous chloride is then converted into metallic copper by replacement with iron.

The process is based on the reaction described by Wohler between sulphur dioxide and a solution of cupric chloride, in which one half of the chloride is eliminated to form hydrochloric acid, and with the simultaneous formation of sulphuric acid. The reaction may be expressed:

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4.$$

The Hunt and Douglas process consists of the following essential steps:

1. Roasting, if the ore is a sulphide.
2. Extracting the copper from the oxidized ore with dilute sulphuric acid, regenerated in the operation of the process.
3. Conversion of the cupric sulphate into cupric chloride, by the addition of some soluble chloride, such as sodium, calcium or ferric chloride.
4. Conversion of the soluble cupric chloride into the insoluble cuprous chloride by the addition of sulphur dioxide, and with the simultaneous regeneration of acid. The acid being used in the second step to dissolve more copper.
5. Conversion of the precipitated cuprous chloride into cupric oxide or metallic copper on the addition of milk of lime or replacement with iron.

In practically carrying out the process, the matte, or ore if a sulphide, is roasted. With care in roasting one third of the copper should be converted into the sulphate, which is soluble in water. The ore is then leached with dilute sulphuric acid, regenerated in a later stage in the process. The copper content of the ore is therefore dissolved as the cupric sulphate, $CuSO_4$. To the neutral solution of cupric sulphate is then added enough common salt, or other soluble chloride, to convert the copper sulphate in the solution into that of cupric chloride. The amount of copper sulphate being determined, salt is added in the proportion of 58.5 parts of sodium chloride to 63.6 parts of copper contained in the sulphate solution. The salt reacts with the cupric sulphate to form cupric chloride and sodium sulphate:

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4,$$

so that the copper in the solution, after the application of the sodium chloride will be in the form of cupric chloride, containing possibly a little cupric sulphate.

[1] Trans. A. I. M. E., Vols. X and XVI.

Through the clear hot solution of cupric chloride is then driven sulphur dioxide, derived from roasting the sulphide ore. The sulphur dioxide serves to convert the dissolved copper into the form of cuprous chloride, with the liberation of the amount of acid which was previously combined with the copper, and the liberation of one half as much more acid due to the oxidation of the absorbed sulphur dioxide.

The combined reaction between the copper sulphate, salt, and sulphur dioxide may be represented by the equation:

$$CuSO_4 + 2NaCl + 2SO_2 + 2H_2O = 2CuCl + Na_2SO_4 + 2H_2SO_4.$$

It is reasonably certain, however, that the following reaction also takes place, whereby a certain amount of hydrochloric acid is also produced:

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4.$$

The cuprous chloride thus obtained, which is insoluble in water or in a sulphate solution, quickly settles to the bottom of the tank, as a white crystalline powder. The clear acid solution, drawn from the precipitated cuprous chloride, is again applied to the ore, and the cycle repeated as often as necessary to get the desired extraction.

The resulting cuprous chloride, seperated from the solution, may then be precipitated with metallic iron, as metalic copper,

$$2CuCl + Fe = 2Cu + FeCl_2,$$

or with milk of lime, as cuprous oxide,

$$2CuCl + Ca(OH)_2 = Cu_2O + CaCl_2 + H_2O,$$

calcium chloride being formed, which may be used to convert the sulphate of copper into the chloride instead of the salt, or ferric chloride.

By the use of a solvent containing only a small portion of soluble chloride, any silver in the ore is converted into the chloride, but remains in the residue and may be extracted therefrom by solution, amalgamation, or smelting.

The reaction between sulphur dioxide and a solution of cupric chloride goes on slowly at ordinary temperatures, but is very rapid between 80 and 90° C. (176 to 194° F.). Solutions of sulphate of copper, mixed with an equivalent of chloride of sodium, and holding 8 per cent. of copper, after being treated at 90 ° C. with an excess of sulphur dioxide, retain less than 1 per cent. of the dissolved copper, while in the presence of an excess of sulphate of copper and sulphur dioxide, the precipitation of the chlorine from chloride of sodium is nearly complete.

The sulphur dioxide, from the roasting furnace, is sufficiently pure for use. A Knowls pump, connected for the purpose, has proved an efficient means of injecting the heated gas into the liquid.

The acid liquors, when the reaction with sulphurous acid is com-

pleted, have exchanged their bright blue color for a pale green, and now contain in solution an excess of sulphur dioxide which must be got rid of before using it to dissolve a fresh portion of copper. This may be effected by keeping back a small portion of the chlorinated copper solution, and after the reduction of the gas is complete, as may be shown by the changed color and the sulphurous odor of the liquid, adding the reserve portion thereto, by which means the excess of sulphurous acid will be oxidized. The larger part of the cuprous chloride separates during the passage of the gas but a furthur portion is deposited on the cooling of the solution.

The excess of sulphurous acid may also be got rid of by blowing a current of hot air through the liquid after it has been withdrawn from the precipitated cuprous chloride.

Cuprous chloride is quickly transferred into cupric oxychloride by atmospheric oxygen and when dissolved or suspended in an acid liquid is by this means converted into a cupric salt, which may be again reduced to cuprous chloride by the action of sulphur dioxide.

If the ore or roasted matte contains silver, the sulphate of copper, which in well-roasted ore should be about one-third of the copper content, is first dissolved out with water, taking care, however, to add enough of some soluble chloride to chlorinate and render insoluble any sulphate of silver which may be present. From the clear solution thus obtained, after adding the requisite amount of chloride of sodium, the copper is precipitated as already described, by the action of sulphur dioxide. The resulting acid liquor, freed from its sulphur dioxide, is now used to dissolve the oxide of copper in the ore, the process being aided by heat, and if the formation of cuprous chloride is feared a current of heated air may be injected and made the means of agitating the mixture. If the ore contains the silver as metal or oxidized sulphide, the chloride of copper formed is a good agent for bringing it into the condition of silver chloride. This will be found in the residue after the extraction of the copper, together with any gold which may be present; lead as sulphate, oxides of antimony and iron and earthy matters. Cobalt, nickel and zinc, if present, will however be dissolved, and not being precipitated by sulphurous acid, will by successive operations, accumulate in the solutions and may be afterward extracted. From the residues, the silver may readily be extracted by brine, after which the gold, if present, may be recovered by chlorination, or the precious metals extracted together from the residues by amalgamation.

Chloride of silver is soluble to some extent in a solution of cupric chloride, and is then in part carried down with the cuprous chloride in the precipitation of the latter.

The cuprous chloride as obtained by the precipitation with sulphur dioxide is a white coarsely crystalline powder, having a specific gravity

of 3.376 and is nearly insoluble in water. After being washed from the acid liquid, it may readily be reduced by placing metallic iron in the moist cuprous chloride, which should be covered to exclude the air. The action spreads rapidly through the precipitate, so that a single mass of iron, within a few hours, will change a considerable volume of cuprous chloride, around it, into a pure spongy metallic copper. Twice the amount of copper is, theoretically, precipitated by iron from a cuprous than from a cupric solution. 45 lb. of iron will suffice to reduce 100 lb. of copper from cuprous chloride. The ferrous chloride which remains in the solution may with advantage be used instead of sodium chloride for chlorinating subsequent solutions of copper sulphate.

Another method of treating the cuprous chloride, consists in decomposing it, preferably at a boiling heat, with a slight excess of milk of lime. The cuprous chloride is by this means converted into a dense orange-red cuprous oxide, which after being washed from the chloride of calcium in a filter press or otherwise, and dried, may be readily reduced to metallic copper, in a reverberatory furnace. For this reaction, 28.0 parts of quick lime are required for 63.4 parts of copper, and the resulting chloride of calcium may be used instead of sodium chloride or iron chloride for chlorinating solutions of copper sulphate. In this case there will be formed an insoluble sulphate of lime, while the free sulphuric acid of the solution is replaced by hydrochloric acid.

Later, Douglas proposed electrolyzing the precipitated solid cuprous chloride, to deposit metallic copper, and use the chlorine again directly on finely crushed matte. A description of this will be found under Electrolytic Processes, page 347.

The Hunt and Douglas process was in operation for many years on a large scale, until quite recently, at Argentine, Kansas, on copper matte. The description here given, of the practical operation of the process, at Argentine, is by Ottakar Hofmann.

The Hunt and Douglas Process at Argentine, Kansas.[1]—The material treated at the plant of The Kansas City Smelting and Refining Company, at Argentine, Kansas, was a lead-copper matte, averaging:

Copper,	39.55 per cent.
Lead,	12.26 per cent.
Iron,	19.90 per cent.
Zinc,	1.88 per cent.
Manganese,	1.01 per cent
Sulphur,	21.43 per cent.

Silver varied from 200 to 300 oz. per ton.

This matte was first crushed by rock breakers, then pulverized in a Krupp ball mill to pass a 50-mesh screen.

The roasting was done in two Pearce two-hearth furnaces. On the

[1] Ottokar Hofmann, Mineral Industry, Vol. XVII, 1908, p. 296.

upper hearth the temperature was kept as low as the heat developed by the oxidation of the sulphur permitted. No fire was applied except after the ore had passed the whole circle of the hearth and came near to the slot through which it dropped into the lower hearth. There a very gentle fire was maintained to prevent the temperature from falling too low.

The best results were obtained by regulating the roasting on the upper hearth so that the material commenced to ignite when it had moved about 8 ft. from the point at which it had entered the furnace. By observing this precaution the roasting was so much advanced by the time the material had reached the drop-slot that the oxidation of the sulphur did not create more heat. This point in roasting was readily observed by stirring the charge; if the particles thrown to the surface brightened and remained so for a short while the oxidation still evolved heat; but if these particles were of a dead red color and began to darken immediately, it was an indication that, in order to continue the oxidation, heat must be applied. It was found to be of the greatest importance to have the roasting well advanced when the material left the upper hearth. When it was neglected and the speed of the feed increased so that the matte, after having dropped to the lower hearth still created heat by oxidation, the finished product was invariably insufficiently roasted. It was endeavored to maintain a gradually increasing temperature in the lower hearth up to the point of discharge.

In order to regulate the final heat, tests were made at intervals of the material before and after it passed the last fire. The samples were sifted and washed in a small dish to determine if any cuprous oxide had been formed. The presence of cuprous oxide is readily determined by its pink color. It often happened that although the material was free from cuprous oxide before passing the last fire place, it could be plainly detected after passing it. This was always an indication that the fire was too hot. It was important to avoid this condition because by too high a temperature cupric sulphate, of which quite a percentage was formed during roasting, was decomposed into cuprous oxide and sulphuric acid, and the matte was discharged before the cuprous could be oxidized to cupric oxide. This test had to be made, not in order to prevent the loss of acid, because in the Hunt and Douglas process more acid is made than needed, but for the reason that when cuprous oxide is treated with dilute sulphuric acid, only one-half of the copper can be dissolved as cupric sulphate; the other half changes into metallic copper, which being insoluble, will remain in the residues.

Even with the greatest care it was impossible to roast a leady matte free from small lumps. They formed in the very early period of the process before any additional heat was used, but as a rule, being usually porous, they were found well roasted. These lumps, however, were very undesirable in the subsequent operation, as they retarded the solution

of the cupric oxide in dilute sulphuric acid. The roasted matte, therefore, had to be crushed. From the roasters the matte was automatically conveyed to the revolving cooling tables, then fed to a ball mill with 50-mesh screens. From the ball mill it was elevated and conveyed to the storage bins.

Solution.—The dissolving of the cupric oxide had to be done in agitating tanks, it being impracticable to conduct the operation in tanks with filter bottoms. When roasted copper matte is brought in contact with dilute sulphuric acid, or even water, it cements and hardens to such an extent that it cannot be handled with shovels if not previously loosened with picks or bars. This hardening of the material prevents to a great extent the free percolation of the solution; this causes much delay and also makes the discharging of the tank a rather difficult task. Even while charging the agitating tanks, it was necessary that the acid solution be kept in lively motion and that the matte be introduced in a gradual stream and not charged with shovels; otherwise hard chunks were formed.

The dissolving was done in wooden agitating stir tanks, 12 ft. in diameter and 6 ft. deep, provided with a strong hard wood propeller which entered and was driven from above. These tanks were about two-thirds filled with acid solution, containing 9 to 10 per cent. free acid, to which some wash water was added. This acid solution, which resulted in the process, always contained 2 to 2 1/2 per cent. copper. The agitator was set in operation and a jet of steam introduced through a lead pipe entering from above and fastened close to the side of the tank. The roasted matte was then brought from the storage bins in cars, which were half covered and provided with a slot through which, by tilting the cars, the matte could be uniformly charged into the tank. The addition of matte to the dilute sulphuric acid produces considerable heat, which aids the solution of cupric oxide and diminishes the amount of steam required to maintain the pulp at the desired temperature.

After a certain amount of matte had been added, the pulp was frequently sampled; these samples were filtered and the filtrate tested for free acid. When the solution was nearly neutral the charging of the matte was stopped, but the agitation continued until the solution became neutral, or almost neutral. This operation was performed with care in order to avoid an excess of matte, which would have enriched the residues with copper. In mixing the acid solution with wash water, care was taken to have enough free acid present so that the resulting solution would contain from 6 per cent. to 7 per cent. copper.

The neutral solution, together with the residues, was discharged through an outlet near the bottom of the stir tank, in a large lead-lined cast iron pressure tank; thence under an air pressure of 40 lb. it was forced through large filter presses with 4×4 wooden plates. When

charged, each press was capable of holding 5 tons of residues. When a press was filled, compressed air was applied to blow out as much as possible of the strong solution which had been absorbed; then the residues, while still in the press, were washed with water.

Below the presses there were two rows of tanks, one to receive the strong liquor, the other the wash water. Some of the tanks were assigned to the stronger portion of the wash water which went back to the process, while the remainder were used as collecting and settling tanks for the weak wash water; this was sent to scrap iron tanks for the precipitation of the contained copper. The strong liquor and strong wash water tanks were connected with a pressure tank, placed on a lower level, by means of which the liquid could be forced to the stir tank level. On opening the filter presses the washed residue cakes dropped into wooden push cars; they were then wheeled to an opening in the press floor, through which they were dumped directly into railroad cars. The residues, which were rich in silver and lead, were delivered to the lead smelting department.

The next operation was to chloridize the sulphate solution. For this purpose the strong solution was elevated, by means of a pressure tank, into a stir tank used only for this purpose. The solution was tested for copper, its volume measured, the total copper in the charge calculated, and as much common salt added as was required to convert the copper present into cuprous chloride (58 parts of sodium chloride to 63.4 parts of copper). The solution was agitated, heated, and then discharged into storage tanks; from these tanks the chloridized liquor was elevated and charged into so-called reducing towers for the treatment with sulphur dioxide.

Precipitation of the Copper with Sulphur Dioxide.—The towers in which this part of the process was carried out were made of steel and lined with lead; the bottoms were cone-shaped. There were four towers. The tops were tightly closed, provided with manholes, inlet pipes for the solution and an outlet pipe for the gas. The cone-shaped bottoms were provided with gas inlet pipes, a steam pipe and a discharge pipe. The outlet for the gas was connected with a main pipe which discharged into a wooden stack. The gas from each tower passed directly into the stack. This arrangement caused considerable loss of gas. By tests it was found that a gas which on entering a tower contained 7 per cent. sulphur dioxide, contained 4 per cent. when discharged, so that there was a loss of 57.1 per cent. Two towers were then connected up so that the gas, after passing through the first, was made to pass through the next tower. By this alteration the loss of gas was reduced to 25.4 per cent., equal to an increased utilization of 31.7 per cent. This experiment demonstrated that the precipitation of the copper in the tower under pressure was correspondingly quicker than in those without pressure.

The gas was furnished by three revolving cylindrical furnaces, of which two were kept in operation and one in reserve. These furnaces were lined and provided with ribs for continually raising the ore and dropping it in a shower. The front end of the furnace was closed, but the cover was provided with air registers and two discharge openings for the roasted ore; the latter opened and closed automatically at each revolution of the furnace. The back end of each cylinder projected a few inches into a small dust chamber, which again was connected with a system of dust chambers. Through the roof of the small chamber, in a slanting position, entered the feed pipe of the furnace. The feeding was done by a very short screw conveyor which could be regulated. The material consisted of iron pyrites concentrates, rich in gold, from Colorado.

The dust chamber was connected with a heavy lead pipe about 4 in. in diameter and was strengthened with iron rings, to which the pipe was fastened. The entire length of this pipe, about 150 ft., was cooled by a spray of water so that the gas was cooled before it entered the pumps. There were two double acting gas-pumps of which, however, one was sufficient to do the work, while the other was kept in reserve. The cylinder measured 27.5 in. in diameter and the piston had a stroke of 28 in. so that each stroke furnished about 19 cu. ft. of gas. The speed had to be regulated so as to get a good roast of the concentrates, and at the same time produce as strong a gas as possible. In order to fulfill both conditions, it was found that the resulting gas could not contain more than 5 per cent. sulphur dioxide. Frequent gas tests had to be made in order to maintain this percentage. Sometimes there was an increase in strength up to 7 per cent., in which case the roasting was not satisfactory; but more frequently it dropped below 5 per cent., which caused a slower precipitation.

The pumps forced the gas through a lead lined receiver, in which a great deal of sulphuric acid condensed and had to be drawn off daily. The gas entered the tower under a heavy perforated lead cone which divided it into small bubbles. Cuprous chloride was precipitated in white crystals, while sulphuric acid was set free. The reaction was most energetic in the beginning while the solution was neutral or contained only a small percentage of acid, became more sluggish in proportion as the percentage of acid increased, and stopped entirely when the copper contents of the liquor was reduced to 2 or 2 1/2 per cent. This remaining copper could not be reduced no matter how long the charge was kept under treatment with the gas. The acid continued to increase slowly, but the copper did not diminish. It is possible that the formation of hydrochloric acid accounts for the copper not being precipitated. The more hydrochloric acid there is formed, the more copper will remain in solution. The hydrochloric acid dissolves cuprous chloride.

Sodium chloride as a chloridizer for the sulphate solution is not the most suitable chemical for the process, as a large quantity of sodium sulphate is formed which goes into solution. As it is necessary to use the solution over and over again, on account of the sulphuric acid which is formed therein, more and more sodium sulphate is formed. In a short time the solution becomes saturated with this salt so that it crystallizes out whenever conditions are favorable. This happens at different stages of the process, causing much annoyance and lessening the merit of the process. It was especially aggravating in the operation of the filter presses. When the matte residues, together with the strong liquor, were forced into the presses, the filtration in the beginning was free and satisfactory, but soon grew less so until it finally stopped entirely, although the press was not one-quarter filled with residues. On opening the press it was found that the chambers were partly filled with a sloppy mass containing many fine crystals, while the filter cloth was densely covered with them. The only way of cleaning the press was to force water through it. This not only caused much delay, especially as this application of water had to be repeated, but caused the making of a large quantity of wash water, from which the copper had to be precipitated with scrap iron. Sometimes it happened that the press could be filled without any trouble, in fact the chamber filling was quite firm; but as soon as water was used to wash the residues the filling shrunk in volume, and the frames which previously were quite full, after washing were only a little over half filled.

Calcium chloride, formed in converting the cuprous chloride into cuprous oxide by boiling with milk of lime, was then tried. The resulting calcium chloride solution, however, was not strong enough to be used directly, containing only 9 per cent. chlorine; it was therefore concentrated. In using calcium chloride, cupric chloride and calcium sulphate were formed, the latter being precipitated. Though this chloridizer made necessary an additional filter press operation, to separate the calcium sulphate from the solution, it was by far preferable to salt, as it left a clean solution, free from undesirable salts. It was found, however, that a sulphate solution, chloridized with calcium chloride, only about half of the copper in solution could be precipitated as cuprous chloride with sulphur dioxide. When the change from salt to calcium chloride was made, a new acid solution, free from sodium sulphate, was used. Several attempts were made with the same unsatisfactory results. It was finally decided to add salt to the new solution and the results were at once better. From that time on chloridizing was done so that three-fourths of the required chlorine was derived from calcium chloride and one-fourth from sodium chloride. After adopting this proportion there was but little trouble with the presses; the filtration was free.

The calcium chloride solution obtained in converting the cuprous chloride into cuprous oxide by boiling with milk of lime, was concentrated by preparing milk of lime with water, allowing the lime to settle, decanting the clear water and replacing the same by weak calcium chloride solution. The condition of the slacked lime was not changed and by repeating this procedure the proportion of calcium chloride in the solution was increased from 9 per cent. to 24 per cent.

When the precipitation in the towers was completed, the cuprous chloride, together with the acid solution, was discharged into a system of seven cone-shaped lead-lined iron tanks. These tanks were so arranged that the liquor flowed from one to the other, and from the last into special charge tanks, to be in readiness to dissolve a fresh lot of matte. These cone-shaped tanks served a double purpose; to give the cuprous chloride an opportunity to settle, and to cool the solution. This liquor when hot holds in solution a large amount of cuprous chloride which precipitates out as the temperature falls. The temperature of the liquor in the first cone was 56.5° C., and in the six following cones it was, 48.0, 47.0, 45.0, 39.5, and 37.0° C., so that the temperature of the last cone was 19.5° lower than that of the first. The cooling proved to be sufficient, as no further precipitation took place in the storage tanks.

Below the level of the cones were three vacuum filters, into which the former could be discharged by opening the bottom valve. Into these filters the cuprous chloride was allowed to drain, then receiving a thorough washing. The washed precipitate was then converted into cuprous oxide.

Conversion of the Cuprous Chloride into Cuprous Oxide.—The conversion was done with milk of lime. The lime was slacked in a flat box and collected in settling tanks. From these tanks the milk of lime of proper consistency was charged, by means of a steam syphon, into a stir tank and heated with a jet of steam. The washed cuprous chloride was gradually charged; its color changed from white to red. Cuprous oxide and calcium chloride were formed. As calcium chloride dissolves cuprous chloride, the calcium chloride which was formed in proportion as the conversion progresses will dissolve some of the freshly charged cuprous chloride. On this property of calcium chloride was based the test by which the conversion is conducted. After a certain amount of cuprous chloride had been added to the milk of lime, charging was interrupted, the stirrer, however, being kept in motion. About 10 minutes later, a sample was taken in a wide necked bottle suspended by a copper wire. Part of this sample was filtered and nitric acid and then ammonia added to the filtrate. If the blue color appeared, some cuprous chloride was still dissolved in the calcium chloride solution. The agitation was then continued for 15 or 20 minutes, when another sample was taken. If the blue color appeared again, more milk of lime was gradually added

and at intervals. After each interval a test was made until the blue color ceased to appear. The last part of the operation had to be conducted carefully to avoid an excess of lime.

The pulp consisting of cuprous oxide and calcium chloride was forced, by means of a double acting pump, into a Johnson iron filter press, where it was washed. The cakes were dumped on a lower floor and dried on steam slabs. When dry, the cuprous oxide was carted to the copper smelting department and dumped into bins conveniently arranged on the charge floor of a cupola furnace. In this furnace it was reduced to metallic copper.

The cuprous oxide always contained from 4 to 5, and sometimes as much as 11 oz., silver per ton. Some of the silver undoubtedly came in with fine particles of matte residues, which were still suspended in the solution when it was charged into the towers for treatment with sulphur dioxide, although the resulting cuprous chloride was clear white and did not show any coloration. However, after more settling tanks were inserted for the solution, the cuprous oxide contained considerably less and more uniform amounts of silver. A sample of cuprous oxide containing 6.25 oz. silver per ton, when leached with a solution of sodium hyposulphite, still contained 5.5 oz. silver per ton, so that only 0.75 oz. per ton could be extracted by that solution. This test was made with cuprous oxide produced before the additional settling tanks were in use; afterward the cuprous oxide did not contain over 2 to 3 oz. silver per ton. The resulting calcium chloride solution gave with sodium sulphide a dark precipitate which consisted mostly of lead sulphide, with only a trace of copper and no silver.

In smelting the cuprous oxide in the cupola, very strong and offensive fumes were formed. These fumes were white, but when very strong assumed a reddish tinge. They consisted chiefly of volatilized cuprous and cupric chloride, some hydrochloric acid and flue dust of cuprous oxide. An investigation showed that the cuprous oxide still contained 1 to 2 per cent. chlorine, notwithstanding the fact that it was subjected to a very thorough washing in the press. This chlorine could not be removed or reduced even by an extended washing. This was not due to the presence of cuprous chloride, caused by an insufficient quantity of lime being used in the conversion, for, even if for the sake of information an excess of lime was used and an unusually long time given for conversion, the above stated percentage of chlorine was always found in the cuprous oxide.

The obnoxious character of the furnace gases was destroyed by passing them through a shower of milk of lime. A tower was arranged which was provided at different levels with strong wooden grates. At the foot of this tower tanks were arranged for making and receiving milk of lime. Two of these receiving tanks were connected with a force

pump. The flue was connected with the wooden tower. Coarse lime rock was placed on the different grates to detain the milk of lime in its downward course as long as possible. At the top several perforated pipes, through which the milk of lime was forced by means of the pumps, were so arranged as to furnish an even spray. The bottom of the tower was made tight and the outlet made to convey the stream into one of the other tanks, so that the milk of lime could be passed through the tower as often as desired.

The effect of the milk of lime was very gratifying. The strong offensive odor of the gases disappeared entirely. The color of the milk of lime turned gradually darker and became finally olive green and very rich in copper. No copper escaped with the gases. When the above green pulp was filtered the filtrate contained 11/2 per cent. to 2 per cent. chlorine. The evaporation was great and water had to be added frequently to maintain the same volume of precipitate. This method proved itself successful and was finally permanently installed.

Treatment of the Wash Water.—In the course of the process a great deal of wash water was made, principally from washing the copper matte residues and the cuprous chloride. The latter, which contained from 1 to 2 per cent. copper, was collected in a number of large tanks, from which it was drawn to be subjected to special treatment for recovering the copper. Wash water containing 2 per cent. copper and as much as practicable of the weaker portion, went back to the process and was used instead of water.

To produce a clean cement copper free from chlorine, a trough was constructed, in sections, about 200 ft. long and 12 in. wide and 14 in. deep. All sections were placed horizontally, but each succeeding one was placed three inches lower. The outlet of each section was two inches lower than the inlet. In some of the sections the compartment was made by inserting across the width of the trough two boards 6 inches wide. These were placed about 12 in. apart to allow for the insertion of a steam jet. This part of the trough was tightly covered for 2 ft. on either side of the jet to prevent the solution from being splashed out by the steam. The 200 ft. of trough was arranged in U shape to avoid too long a building, and to make the handling of the material easier. After passing through the last section, the solution flowed through a few scrap iron tanks to precipitate any copper which might be present as sulphate. Each section of the long trough was charged about 4 in. deep with cement copper, evenly spread. The wash water from the main department flowed into a circular tank 8 ft. in diameter and 5 ft. deep, thence through an overflow into the first section of the long trough. The purpose of the circular tank was to heat the wash water by means of steam jets before it entered the long trough. It gave an additional, though not very effective, opportunity for the settling of particles of matte

residues which might not have settled in the proper wash water storage and settling tanks. As the wash water resulting from the different operations of the process contained cupric sulphate in addition to cupric chloride, salt water was added to the storage tanks to convert the cupric sulphate into cupric chloride.

By passing the wash water through and over the cement copper the copper was precipitated as cuprous chloride. Once a day the cement copper in the troughs was gently worked in order to bring fresh particles to the surface. At one side and below the level of the troughs, a revolving barrel, 10 ft. long and 6 ft. in diameter was erected; when a large part of the cement copper in the troughs had changed to cuprous chloride, it was removed from the troughs and charged into the barrels, to which small scrap iron, water and salt were added. By means of a steam pipe, the pulp was slightly heated to start the reaction; then the steam was turned off. This pipe entered the barrel through one of its axles and was bent downward to reach into the pulp; it was kept in position by a stuffing box. Very soon an energetic reaction took place; the heat developed causing the pulp to boil violently. The steam found an outlet through another pipe inserted through the opposite axle. The salt was added to dissolve some of the cuprous chloride; this caused the reaction to start more quickly. The cuprous chloride changed to cement copper and the iron into ferrous chloride. The latter had the same effect as salt and dissolved cuprous chloride, thus assisting the process.

After the steam ceased to escape, the barrel was stopped and a sample taken. The sample was filtered and the filtrate tested. When the blue color could no longer be obtained with nitric acid and ammonia, the pulp was ready to be discharged. The conversion was completed in from 6 to 10 hours. Below the barrel was a square tank, with a filter bottom, fitted on two opposite sides with rails which extended beyond the tank. On this track was an 8-mesh screen fastened to a wooden frame and provided with four wheels. The screen covered the whole top of the tank. In discharging the barrel, the copper cover of the manhole was removed and the barrel gradually turned by means of a crow-bar. When the charge was out, the inside of the barrel was rinsed with water. The screen retained pieces of iron, while the cement copper and solution passed through to the filter tank. By means of a stream of water, the iron on the screen was separated from adhering cement copper and returned to the barrel to serve as part of the next charge. The screen on wheels was pushed away from the tank, the outlet under the filter opened, and the iron solution allowed to drain off. Then warm dilute sulphuric acid was permitted to flow in. As soon as the acid appeared at the outlet the latter was closed. The acid was applied to remove basic salts, to prevent their formation as far as possible, and to dissolve any small pieces of iron which had passed through

the screen. After several hours the acid was removed to a special tank to be used again. The copper was then thoroughly washed in the tank to free it from acid. The resulting cement copper was of a very clear color and unusually pure, containing 99 per cent. copper and but a trace of arsenic. It was melted in the refining furnace.

This method gave such good results that three more barrels were erected. The method eliminated the conversion of cuprous choloride into cuprous oxide by the milk of lime, the smelting of the product in the cupola furnace, the treatment of the furnace gases, the very unclean manipulation of the scrap iron tanks, and the additional treatment of the cement copper to free it from cuprous chloride.

Modification of the Hunt and Douglas Process.—To simplify the operations and to avoid the saturation of the solution with sodium sulphate and its attendant disadvantages, Hofmann worked out and successfully introduced the following modus operandi:

1. The process was started with a stock of dilute sulphuric acid. By treating the roasted matte in the usual way in the stir tanks, a clean sulphate solution was obtained which filtered well in the presses.

2. The sulphate solution was chloridized with hydrochloric acid, of which in starting, a stock on hand was required. By chloridizing the sulphate solution with hydrochloric acid, cupric chloride is formed and sulphuric acid set free. No foreign salts are introduced and the solution remains clean, while by chloridizing with sodium chloride the solution becomes quickly saturated with sodium sulphate.

3. The cupric chloride solution containing the liberated sulphuric acid was then treated in a stir tank with cement copper. The cupric chloride by the action of metallic copper is reduced to cuprous chloride, while the sulphuric acid remains unchanged. A steam jet is used to hasten the reaction. An excess of cement copper serves the same purpose. When the filtrate of a sample shows no reaction for copper, the operation is completed and the pulp is drawn into a pressure tank and forced through a filter press. The filtrate, which is now a clean sulphuric acid solution, is elevated to storage tanks, whence it is used as required to dissolve the cupric oxide of a new lot of roasted matte. To produce as little wash water as possible, the solution absorbed by the matte residues and by the cuprous chloride is forced out by compressed air; this works very well, as the filtering capacity of both materials is not lessened by the formation of crystals. For the same reason the subsequent washing is quickly done, requiring comparatively but very little water to accomplish it.

4. The washed cuprous chloride was treated in revolving barrels in the same manner as described above, but care was taken that no more water was added than necessary, so that as strong a ferrous chloride solution was produced as practicable.

5. The ferrous chloride solution was evaporated in the same iron pans which were formerly used for concentrating the calcium chloride solution.

6. The solid ferrous chloride was charged into retorts, which were provided with water for steam and air. When heated heavy fumes of hydrochloric acid were formed; these were passed through a cooling arrangement, in which a large portion was condensed. This condensed acid was strong and contained 35.6 per cent. chlorine. The acid fumes which were not condensed were made to pass through two towers made of stoneware pipes and filled with coke. The gas escaping from the first tower entered at the bottom of the second. To avoid the accumulation of too much water in the stock solution, cupric sulphate solution was used instead of water as a spray for the coke, thus chloridizing the solution. The solution, as a rule, after passing through the towers, contained an excess of hydrochloric acid. This condition, however, was properly adjusted by adding sulphate solution before the treatment with cement copper.

7. The resulting cement copper was very pure, containing from 90 to 94 per cent. and more copper. This was smelted in a refining furnace; no obnoxious fumes were evolved as in the case of cuprous chloride. There was, of course, a loss of sulphuric acid as well as of hydrochloric acid which was caused chiefly by the wash water; these had to be replaced from time to time to keep up the volume of stock solution. However, this shortage was not great and the loss of replacing it was far less than that of the eliminated operations.

This modified process was used for some time until Hofmann received instructions from the company for the necessary alterations of the works to prepare for the more profitable manufacture of blue vitriol. This was done by Hofmann's method of producing this material direct from the roasted copper matte, described in chapter 18.

Copper Extraction at Falun, Sweden.[1]—The old copper mine at Falun produces two classes of minerals known as hard and soft pyrites respectively. The former, consisting of mixtures of quartz and copper pyrites, contains about 3 1/2 per cent. and the latter, which is mainly composed of iron pyrites, about 1 per cent. of copper. The hard ore is roasted in heaps, about 10 per cent. of the sulphur being driven off, while the soft pyrites is treated in sulphuric acid works, about 30 per cent. of the sulphur being utilized.

The burnt residues, to the extent of about 45 tons hard, and 12 tons soft, per day, are mixed with 14 and 10 per cent. of salt respectively, and ground in ball mills. The hard ore mixture is then subjected to a chloridizing roasting in a White-Howell roasting furnace, in which

[1] *E. and M. J.*, Aug. 30, 1902; Berg and Huttenmanische Zeitung, 1902.

15 tons are roasted in 24 hours. The soft ore is roasted in a double bed roaster in which 7 tons are worked through daily.

When complete chloridization has been effected, the roasted material is transferred to wooden vats, where the cupric chloride is dissolved out by weak sulphuric or hydrochloric acid, the latter being obtained by condensing the waste gases from the roasters.

After the ore has been treated with the dilute acid solution, it is washed with clear water. The wash water is pumped back and used as a second liquor on a following charge.

The solution from the ore contains all the copper, bismuth, selenium and silver, together with a portion of the gold contained in the ore. The remainder of the gold is extracted later by washing the residues with chlorine water.

The copper solution is precipitated by scrap iron as cement copper, which, together with the associated mud and iron salts, is smelted and granulated for conversion into copper sulphate by means of dilute sulphuric acid and air in the ordinary way.

The residual mud from the copper sulphate crystallizers, containing gold, silver, selenium, and bismuth is dried and smelted with litharge, soda and sawdust to collect the precious metals into lead. The gold-bearing solution from the chlorine extraction is reduced by adding a portion of the original copper extracting solution containing ferrous chloride, which reduces the chloride of gold, producing metallic gold and ferric chloride. The gold so obtained is extremely finely divided, and an addition of lead acetate and sulphuric acid is necessary to obtain a sufficiently dense precipitate. The gold precipitate is smelted with lead in much the same as the copper precipitate. The wasted liquor from the copper extraction is worked up for ferrous sulphate, which by roasting, gives a red ferric oxide, which is used for paint.

The annual production of the works is as follows:

Copper sulphate,	1,600 tons
Ferrous sulphate,	300 tons
Iron oxide, red paint,	1,000 tons
Silver,	400 kilograms
Gold,	100 kilograms

The Bradly Process.[1]—In the Bradly process the sulphide ore is carefully roasted, in what he calls an amphidizer, which consists of a rotary drum with a central heating flue through which [illegible] be supplied. The rotation of the drum operates to [illegible] and air through the drum in one direction and [illegible] to the same end, so that the copper is more [illegible] phated and the iron oxidized. The roasting

[1] *E. and M. J.*, Jan. 6, 1912: U. S. Patent 1,011,56

perature of from 450 to 550° C., air being blown into the apparatus to hasten the oxidation.

The roasted ore is then treated with an excess of calcium chloride solution in a reaction drum, while the temperature is maintained at about 100° C. Cupric chloride is produced by the reaction between the copper sulphate and calcium chloride, while any ferric sulphate in the ore, due to the roasting, reacts with calcium chloride to produce ferric chloride. The calcium sulphate resulting from both these reactions is insoluble and is separated by filtration in the succeeding step. The production of ferric chloride at this point is advantageous in that it dissolves copper oxide, copper sulphide or metallic copper, which remained unaffected by the roasting, producing copper chloride, and this ferric chloride also maintains the copper chloride in the cupric condition.

The gold and silver in the ore are brought into solution by converting all the copper into cupric chloride and then adding a small amount of chlorine, chlorous, or chloric compounds. The chlorides of silver and gold being soluble in calcium chloride solutions may afterward be precipitated with the copper and subsequently separated. After leaving the reaction drum the mass of gangue, solution, and precipitates is subjected to filtration. The solid matter forms a cake which consists of the gangue in the ore except a small amount of iron and alumina which have been taken into solution and the calcium sulphate precipitate already mentioned. The solution comprises a carrier in which has been dissolved the metals to be recovered, a small amount of iron and alumina and any zinc which may have been in the ore; the arsenic will have been separated by filtration, as it has been rendered insoluble. The solution is then subjected if necessary to a further oxidizing operation in order to be sure that the metals are all combined at their highest valency.

The solution is then in condition for treatment for the separation of the dissolved metals. The precipitation of iron and alumina may be made by cupric oxide, hydrate or calcium carbonate, and as this precipitate will carry some copper it is returned to the amphidizer, or roasting furnace, after having been removed from the solution by filtration. In the amphidizer the iron and alumina in the precipitate are rendered insoluble, while the copper is left in a soluble condition and can be recovered. The solution from which the iron and alumina has been removed and which then contains the bulk of the copper is run into a second tank in which the copper is precipitated by carbonate of lime as oxide of copper. This precipitate is filtered from the solution and the copper is recovered by further treatment such as by reduction in an ordinary smelting furnace.

Any silver and gold in the solution is carried down during the precipitation of the iron, aluminum, and copper, and finally recovered by separation from the latter metal. Zinc contained in the ore passes into solution as chloride of zinc and accumulates. It is therefore necessary

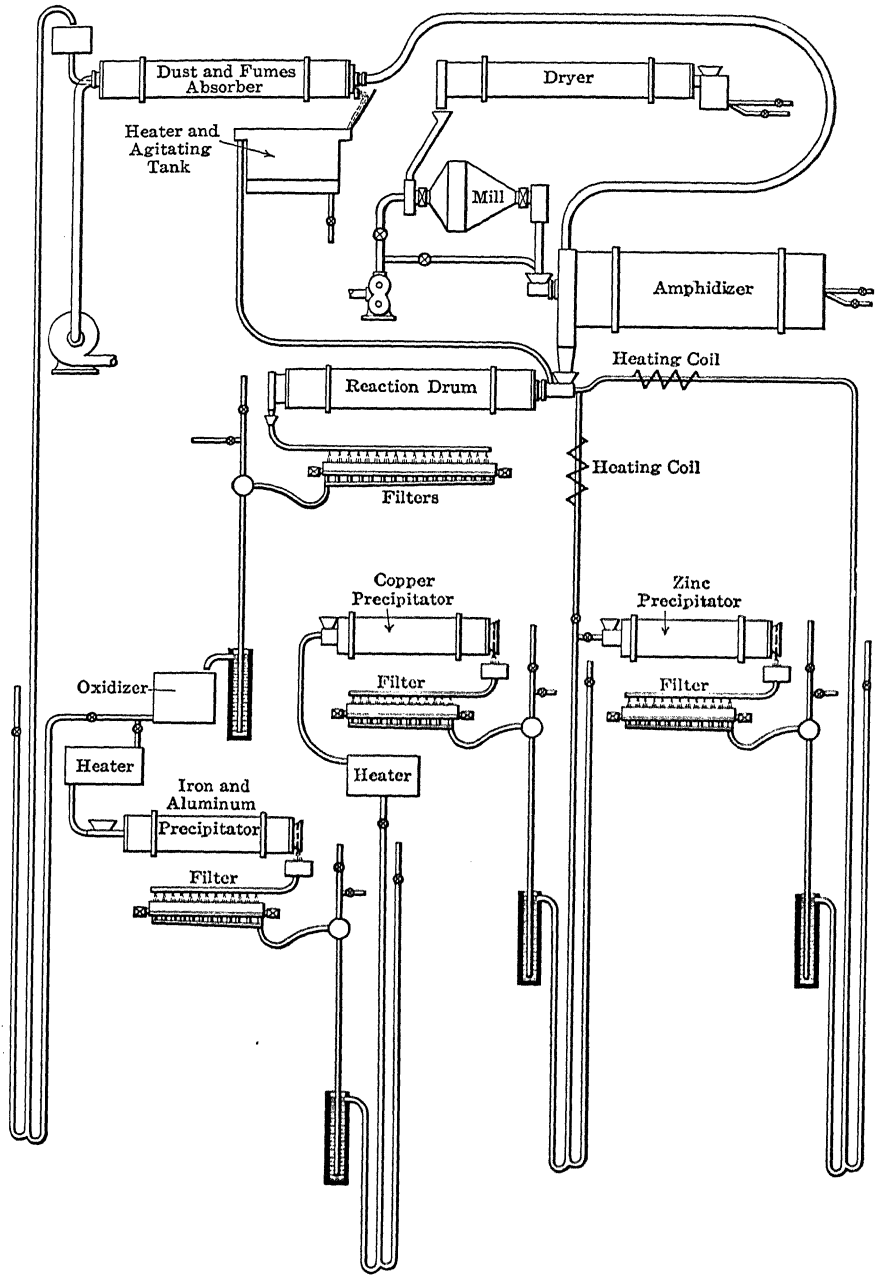


FIG. 48.—Bradly process. Diagrammatic sketch.

at stated times to run the solution, or a part of it, after the final treatment and before returning it to the reaction drum, to a third precipitator in which the zinc is precipitated by means of caustic lime. The regenerated solution from which the gangue and all metallic compounds has been removed and which contains calcium chloride is returned to the reduction drum for the treatment of additional ore from the amphidizer, thus completing the cycle.

During the roasting considerable dust and fumes are given off, containing sulphurous and sulphuric anhydride. This is condensed by a portion of the solution diverted from the main stream, after filtration from the ore, and is again returned to the reaction drum.

Fig. 48 shows a diagrammatic sketch of the Bradly process.

Longmaid-Henderson Process for Treating Pyritic Cinders.—(The descriptions of the early work of this process, and of European practice, are principally by Clapham, Wedding, Ulrich, Gill and Lunge; the descriptions here given is taken largely from Lunge's Treatise on the Manufacture of Sulphuric Acid and Alkali, Vol. 1, 1891.)

Sulphuric acid is largely made from pyritic ores, many of which contain copper worth recovering, after the sulphur has been roasted off as sulphur dioxide for the sulphuric acid works. Such ores are quite widely scattered, but the largest and most valuable deposits occur in Spain. From the Rio Tinto mines in Spain the ore is shipped to many of the commercial and manufacturing nations of the world. During the year 1874, there existed in Great Britain alone 22 copper works in which 450,000 tons of pyritic cinders were treated annually by wet methods for the extraction of the copper. Two of these works made sulphate, three produced refined copper, and the rest sold their cement copper precipitate to copper refineries. In 1882 the quantity of pyritic cinders treated for copper in Great Britain amounted to 434,427 tons, containing 15,300 tons of copper.

The process used in England at that time is still largely in use to-day, both in Europe and the United States, and with very little modification from the original process.

The Longmaid-Henderson Process consists essentially of roasting the pyritic cinders, from the sulphuric acid works, with salt, leaching out the chloride of copper so formed, followed by precipitation with iron. Longmaid obtained a patent dated October 20, 1842, and another in January, 1844, both relating to the treatment of pyritic cinders by roasting with salt. Longmaid described the principles of the process very much as it is carried out to-day, certainly with a view of making salt cake and chlorine as the principal products, and he worked it out on a large scale; so that he must be regarded as the founder of the wet extraction of copper. Gossage, in 1850, first employed sponge iron for precipitating the copper. Henderson carried the process to greater perfection. In

1865 he erected a plant at Hebburn for the Bede Metal Company, to extract copper from pyritic cinders, the process of which he had protected by patent. Henderson's principal improvement was the introduction of absorption towers through which the acid gases from the chloridizing roasting were condensed and yielded a weak acid solution, which was then used in leaching the copper.

The most important ores treated by this process, in English works, were from Spain and Portugal, and contained from 47 to 49 per cent. sulphur; from 3.50 to 3.80 per cent. copper and from 0.75 to 1.20 oz. in silver, per ton.

In the German works, at Oker, the ordinary copper ores treated by this method contained 60 per cent. iron pyrites, 23 per cent. copper pyrites, 6 per cent. blende, 2 per cent. galena, and 9 per cent. gangue.

The steps in the process may be summarized as follows:

1. Mixing the ore with salt and then grinding the mixture.
2. Chloridizing roasting.
3. Leaching the roasted ore.
4. Precipitating the silver from the argentiferous liquors.
5. Precipitating the copper from the desilverized liquors.
6. To which may be added, the preparation of the residue, rich in iron, for the iron smelters. This is usually done at the copper works.

The percentage of sulphur in cinders as supplied by the acid works to the copper extraction plants varies from 2 to 10 per cent. A fair average may be considered from 4 to 5 per cent. At Oker the cinders contained from 5 to 8 per cent. sulphur and from 6 to 9 per cent. copper.

The following analyses by Gibb shows the composition of the pyritic cinders as the copper works received them:

	Rio Tinto	Tharsis	San Domingo	Ytteron (Norway)
Copper, Iron, Sulphur } Calculated as Cu_2S and FeS_2	1.65 3.64 3.53	1.50 3.23 3.15	1.55 3.76 3.62	1.01 3.33 3.10
Cupric oxide	2.75	2.56	2.70	0.39
Zinc oxide	2.02	0.55	0.47	6.46
Lead oxide	0.47	0.70	0.84	0.06
Silver	0.0037	0.0023	0.0023	
Cobaltic oxide	0.007	0.032	0.33	
Bismuth oxide	0.013	0.010	0.013	
Calcium oxide	0.20	0.25	0.28	2.30
Ferric oxide	77.40	77.00	78.15	68.06
Sulphuric acid	6.10	5.25	5.80	6.56
Arsenic acid	0.24	0.17	0.25	0.05
Insoluble residue	1.45	5.85	1.85	8.74
	99.46	100.25	99.31	100.06

Philips gives the following as the composition of cinders from San Domingo ore:

Sulphur,	3.66
Arsenic,	0.25
Iron,	58.25 (83.0 Fe_2O_3)
Copper,	4.14
Zinc,	0.37
Cobalt,	trace
Lead,	1.24
Lime,	0.25
Insoluble,	1.06
Moisture,	3.85
Oxygen and loss,	26.93

Samples from Widnes and Hebburn showed,

	Widnes	Hebburn
Copper,	4.08 per cent.	5.75 per cent.
Sulphur,	4.12 per cent.	3.75 per cent.

Of this there was soluble in water,

Copper,	46.0 per cent.	26.1 per cent.
Sulphur,	43.0 per cent.	37.0 per cent.

Soluble in hydrochloric acid,

Copper,	22.2 per cent.	13.3 per cent.
Sulphur,	55.0 per cent.	59.0 per cent.
Copper insoluble in water and HCl,	31.8 per cent.	60.6 per cent.

The ores that used to be treated at Oker, showed, on an average of a month's run:

Copper (principally as CuO),	7.83 per cent.
Iron (principally as Fe_2O_3),	40.53 per cent.
Lead (as PbO),	2.09 per cent.
Silver,	0.008 per cent.
Zinc (as ZnO),	1.95 per cent.
Manganese (as Mn_3O_4),	0.40 per cent.
Sulphur,	3.80 per cent.
Sulphuric acid (corresponding to 3.8 per cent. S.,	9.51 per cent.
Alumina,	4.43 per cent.
Other gangue,	11.65 per cent.

The pyritic cinders as received by the copper extraction works, were first finely ground to about 8 or 10 mesh and at the same time mixed with a sufficient quantity of salt. In hand furnaces the amount of salt varied from 10 to 20 per cent. but in mechanical furnaces it was less—about 7 1/2 per cent. At Oker the cinders were mixed with 15 per cent. carnallite, which contains chlorides of magnesium, potassium, sodium, and calcium; all of which assist in the chloridizing roasting.

The chloridizing was done in reverberatory, and in muffle fur-

naces. Sometime in a sort of combination between the two, in which only a part of the furnace was muffled. See Figs. 10, 11, and 12, pages 98 and 99.

The chloridizing roasting of these cinders is in detail essentially the same as described in the chapter on chloridizing roasting. Whatever the means of furnace employed, the object to be attained is to sufficiently convert the copper into sulphate, which owing to the presence of the chloride salts, at once forms with the cupric sulphate, by mutual decomposition, cupric chloride and sodium sulphate. The iron should be converted as completely as possible into the ferric oxide, so as to be insoluble both in water and dilute acids.

In roasting, the SO_3 and O acting upon NaCl, chlorine is evolved which greatly aids in chloridizing the copper as well as any other metals present. At the same time a large quantity of hydrochloric acid is formed which converts the oxides of copper, silver, zinc, etc., into chlorides, while at the temperature of the roasting furnace ferric chloride cannot exist. Since chlorides of copper are both unstable and volatile at very high temperatures, a low red heat ought not to be exceeded; so that any copper pyrites still present in the cinders is not burned, and therefore escapes chloridization.

Wedding describes in detail the roasting at Widnes as carried on in a gas furnace. The charge of 4500 lb. of ore, mixed with 17 per cent. salt, is spread out evenly on the hearth and slowly heated till a low red heat has been reached nearest the fire bridge; the charge is rabbled and left to itself, the gas being shut off but the air allowed to enter, so that after 2 hours scarcely any glowing can be perceived at the fire bridge. After 1 hour's and 3 hours' roasting, respectively, the copper of the charge behaved as follows:

	1 hour's roasting	3 hours' roasting
Soluble in water,	54 per cent.	51 per cent.
Soluble in hydrochloric acid,	38 per cent.	42 per cent.
Soluble in nitric acid,	8 per cent.	7 per cent.

After 3 hours the charge is quite dark, and is now well rabbled. There ought to be no necessity for more fire, as the temperature from first should have been raised to the proper point. The charge is now rabbled regularly at short intervals, and the temperature of itself rises in consequence of the chemical reactions. The rise becomes sensible after 4 3/4 hours, counting from the beginning; so that after 5 1/4 hours a dark red heat is reached. Up to this point there is a copious evolution of white vapors and blue flames; from this period there is less of these, and it is the roasterman's principal task to see that heating of the charge is uniform, and that some places do not show more flame than others. After 6 1/2 hours these flames are almost entirely gone; and this fact,

along with the greenish-gray color of the charge, are the principal tests for judging whether the operation is finished. A sample is now taken, and if its examination shows the completion of the roasting process, the charge, which has now been 6 1/2 or 6 3/4 hours in the furnace, is withdrawn. Of the copper now,

75 per cent. is soluble in water,
20 per cent. is soluble in hydrochloric acid,
5 per cent. is soluble in nitric acid.

In roasting, in order to get the best results, the charge is first heated to a temperature sufficiently high to start the chemical reactions, and then to maintain these at the lowest possible temperature up to the finish, and to see that the entire mass of ore is uniformly treated.

It is of great importance not to leave the ore any longer in the furnace than necessary after the roasting is completed. The depth of the ore is usually from 4 to 5 in., and this depth of charge, while more difficult to rabble, facilitates the chloridization, since the gas rising in the ore heated both at top and bottom has all the more opportunity of coming in contact with all parts of it.

At Oker, where gas-fired furnaces exactly like those at Widnes were used, each charge of 5000 lb. of ore with 15 per cent. carnallite is brought to a low red heat in 4 hours; the firing is then discontinued and the mass rabbled, for 4 or 5 hours with a very low fire or without any, the air valves being meanwhile kept open in order to allow the air to act on the charge. The charge is then withdrawn and a fresh charge introduced as soon as the furnace is empty. Five tons of roasted ore were worked off in 24 hours, with a coal consumption of 10 to 12 per cent. The composition of the roasted ore after chloridizing roasting with 20 per cent. carnallite was as follows:

SOLUBLE IN WATER

	Per cent.		Per cent.
Cu,	3.86	calculated as $CuCl_2$,	8.17
Ag,	0.005	calculated as AgCl,	0.006
Fe,	0.60	calculated as $FeCl_2$,	1.38
Al_2O_3,	0.17	calculated as $Al_2(SO_4)_3$,	0.56
Zn,	1.64	calculated as $ZnCl_2$,	3.42
Mn,	0.75	calculated as $MnCl_2$,	1.71
Ni,	0.07	calculated as $NiCl_2$,	0.15
CaO,	1.60	calculated as $CaCl_2$,	3.17
$MgSO_4$, K_2SO_4 Na_2SO_4,			20.50
			39.066

INSOLUBLE IN WATER

	Per cent.			Per cent.
Cu,	2.57	calculated as	CuO,	3.18
			Cu_2S,	0.03
Pb,	1.17	calculated as	$PbSO_4$,	1.26
Fe,	34.56	calculated as	Fe_2O_3,	47.91
			$Fe_2(SO_4)_3$,	1.02
			FeS_2,	0.18
Al_2O_3,	0.44	calculated as	Al_2O_3,	0.44
Zn,	0.37	calculated as	ZnO,	0.46
Mn-Ni,	trace			
CaO,	0.49	calculated as	$CaSO_4$,	1.19
SO_3,	1.49			
Cl,	trace			
S,	0.64			
Insoluble in acids,				3.69
				60.38

In mechanical furnaces less salt was used than in hand roasters—averaging 7 1/2 per cent. as against 15 per cent. in the hand furnaces. Sometimes only a portion of the salt was added at the start, and the remainder added afterward. In the muffle roasters the ore is first roasted 9 hours with 12 per cent. salt and another 3 hours with 8 per cent. more salt. In the combination furnaces with protecting arch the weight of the ore was 5800 lb., and the time of roasting 8 hours; in the mechanical furnaces 5 tons were roasted in 9 hours.

Gibb investigated the comparative working of the different furnaces, which may be summarized as follows:

	Gas furnace		Muffle furnace		Mechanical fur.	
	Per cent.	Cu. per cent.	Per cent.	Cu. per cent.	Per cent.	Cu. per cent.
Cupric chloride	4.03	1.90	4.25	2.00	6.70 =	3.15
Cuprous chloride	0.32	0.20	0.35	0.21	nil	nil
Cupric oxide,	1.26	1.00	0.88	0.70	0.32	0.25
Sodium chloride	2.50		3.40		0.90	
Sodium sulphate	13.18		17.40		14.03	
Insoluble copper		0.15		0.12		0.13
		3.25		3.06		3.53

The principal object in roasting, of course, is to get as much copper as possible soluble in water or dilute acids. In the above comparison there is a slightly better result in favor of the muffle roaster, but not

enough to give a decided advantage, and the advantage is largely overbalanced by the increased fuel consumption of the muffle furnaces.

At Oker the average results of the constantly taken samples of the chloridized ore showed 75 per cent. of the copper was soluble in water as the cupric chloride and neutral sulphate; 20 per cent. was soluble in dilute hydrochloric acid, as cuprous chloride and oxychloride, and 5 per cent. was insoluble in the treatment of the ore for the copper but was soluble in aqua regia.

In roasting, the sulphur in the pyritic cinders must bear a certain proportion to the copper. With a 4 per cent. copper ore the sulphur should not exceed 6 per cent.; an equal percentage of sulphur and copper is preferable. If less sulphur is present, raw pyrites must be added.

The test for ascertaining the completion of the roasting are made by taking a certain definite quantity of the roasted ore, leaching it with water and dilute hydrochloric acid just as in the regular leaching; the residue is then boiled with aqua regia, supersaturated with ammonia, and allowed to settle; the more or less blue color of the ammonia-cupric salt gives a sufficient indication of the percentage of insoluble copper.

Condensation of the Furnace Gases.—In all but the muffle furnaces the gas from the roasting ore is mixed with gas from the fire-boxes. Even in the muffle furnaces the gases from the ore are mixed with air to such an extent that a condensation of strong acid is not possible. The acid from the muffle furnaces is only slightly more concentrated than from the reverberatories; but this is not a serious matter as the acids are always used in a very dilute solution for leaching. The furnace gases contain principally, besides oxygen and nitrogen, sulphur dioxide, sulphur trioxide, hydrochloric acid, chlorine, and very small quantities of metallic chlorides. Henderson proposed volatilizing the copper entirely as cupric chloride and condense the latter in towers; but this has turned out quite impracticable. The quantity of copper volatilized in the ordinary process of roasting is not large, about 1/4 per cent. of the whole, and this is condensed with the acid in the tower acid for leaching the ore.

The condensation of the gases from the roasters takes place in towers made of brickwork set in tar and sand (or, better, of stone flags), and packed with coke, fire bricks, and the like. Large stoneware pipes are sometimes employed. Coke can be used for the filling material with the muffle roasters; but the other furnaces require brick, or similar material and must have larger condensers, as these towers have to serve for a larger volume of gas. The size of the towers varies with the plant; for 12 furnaces a tower of 8 ft. square and 40 to 50 ft. high is sufficient. The gas enters at the bottom, meets a spray of water coming from the top, which washes the acid out of it, and again leaves the tower at the top, whence it is taken downward into a flue leading to the chimney.

The total condensed liquid, which is a mixture of sulphuric and hydrochloric acids, is used in the succeeding operation of leaching, and frequently is not even sufficient for dissolving all the copper oxide and cuprous chloride. The sulphur dioxide in the liquid is oxidized to sulphuric acid by the action of the chlorine.

Leaching of the Roasted Ore.—The roasted ore is carried in bogies on tramways to the leaching tanks. The material used in the construction of these tanks is wood. It is most difficult to prevent leakage in large wooden tanks when using a hot chloride solution; on this account the entire floor of the leaching shed is covered with a thick layer of asphalt and slopes to one side, so that all liquors can be recovered in a catch-well.

The leaching tanks are square, about 11 × 11 ft. wide, and 4 to 5 ft. deep, made of well seasoned and planed 3-in. planks, secured by corner pieces, screw-bolts, etc. The joints are tightened by putting a little redlead between the planks before putting them together; the bottom joints are best caulked with tarred spun yarn, and the whole tank painted with hot coal tar. At Oker lead-lined tanks were used, but they were very expensive and needed frequent repairing. On the bottom of the tank are placed slats, laid on end; and upon these perforated tiles or boards; upon this false bottom a layer of sifted furnace cinders is spread out, and on top of this a layer of sand, coke, or straw from 3 to 6 in. deep.

The ore is charged upon the bed so prepared and is then ready for leaching. The leach liquors are conveyed in earthenware and india-rubber tubes of 3 to 4 in. in diameter, which are provided with iron pinch-clamps. In order to force the liquors from one tank to the other, or from the catch-well into the tanks, simple stoneware injectors are provided. Each tank has a steam pipe for heating.

In each tank there is put 10 tons of roasted ore, quite hot, from the furnace, and is covered with a weak liquor from a previous operation, which gets heated by the heat of the mass itself. After one or two hours the now concentrated liquor is run off by a plug-hole below the false bottom, and is delivered to the precipitating tanks. The plug is put in again, and the ore leached with hot water; thus weaker liquors are produced which are forced to another tank, as described. Generally three waters are put on, and thus most of the purest copper and 95 per cent. of all the silver contained in the pyrites are obtained. After the treatment with the water the dilute acid solution from the tower is applied, sometimes as many as six applications before all the copper is satisfactorily extracted.

The liquors obtained by use of acid solutions contain many impurities, especially arsenic, bismuth, antimony, and lead—according to Gibb, for each 100 parts of copper, 5.4 arsenic and 0.3 bismuth; these liquors are usually treated separately in most works because they yield impure copper.

As a rule each solution application is allowed to stand only a few hours on the ore; the nine washings of each tank, together with the filling and emptying, takes about 48 hours.

The effect of the leaching is best seen from the following by Gibb, which at the same time shows the difference in work between mechanical and hand-worked furnaces:

Soluble in water	Mechanical furnace per cent.	Hand-worked furnace per cent.
Cupric chloride,	4.16 = 1.96 per cent. Cu	3.81 = 1.82 per cent. Cu
Cuprous chloride,	none	0.19 0.12
Cupric sulphate,	1.83 0.80	none
Ferrous sulphate,	0.15	none
Ferric sulphate,	0.75	none
Zinc sulphate,	2.01	1.95
Calcium sulphate,	1.29	1.39
Sodium sulphate,	9.17	11.13
Sodium chloride,	none	2.64
	19.36 2.77	21.11 1.94
Soluble in dilute HCl		
Cuprous chloride,	0.15 = 0.01 per cent. Cu	0.33 = 0.21 per cent. Cu
Cupric oxide,	0.225 0.18	1.01 0.81
Residue by difference,	80.40 0.08	77.55 0.11
	100.00 3.04	100.00 3.07
Sodium chloride equivalent to sodium salts as above,	7.56	11.81

At Oker, the process is carried out as follows: The roasted ore is leached in charges of 5 tons each, first with the final liquor of a previous charge, 100 parts of this liquor, of 1.145 specific gravity, contained:

Cu,	0.015	CoO; NiO,	0.01
Bi,	trace	CaO,	0.12
FeO,	2.14	MgO,	0.52
Fe_2O_3,	0.15	Alkalies,	2.61
Al_2O_3,	0.11	Cl,	2.56
ZnO,	0.06	SO_3	5.89
MnO,	0.31	As; Sb,	trace

Total solids, 14.49 per cent.

This liquor, already heated in pumping by the injector to 50° C. is further heated, when it comes in contact with the hot roasted ore, to nearly the boiling-point. When the charge is thoroughly saturated with the liquor, the spigot is opened and the liquor allowed to drain as long as it shows any blue color. This lasts from 4 to 5 hours and furn-

ishes a copper liquor of 1.355 specific gravity and of the following composition:

Cu,	3.71	CoO–NiO,	9.04
Pb,	0.01	CaO,	trace
Ag,	0.005	MgO,	0.27
Bi,	trace	Alkalis,	10.60
Fe_2O_3 / Al_2O_3	0.29	Cl,	12.56
ZnO,	4.97	SO_3	8.95
MnO,	0.58	As–Sb,	0.32

Total solids, 42.305 per cent.

After the first leaching is over, the dilute condenser acid, first brought to boiling, is run into tanks and allowed to act for 24 hours; then it is drawn off, and a third leaching effected by sulphuric acid. For 5 tons of ore 250 lb. of chamber-acid of 106° Tw., diluted to 12° Tw. and heated to boiling, is employed and allowed to remain in contact with the ore for two days, or until the liquor acquires a neutral reaction.

The first copper liquors contain most of the silver, and are therefore kept apart from the later liquors, which do not contain as much silver.

The cupric chloride is, of course, easily dissolved in the final liquor; the cuprous chloride in the presence of alkaline chlorides is also dissolved at a higher temperature without difficulty; lastly cupric oxide is to be converted into cupric and cuprous chlorides by the ferrous chloride of the final liquors from previous applications:

$$2FeCl_2 + 3CuO = Fe_2O_3 + CuCl_2 + Cu_2Cl_2$$

but this could only be done by an intimate mechanical mixture of the liquor with the ore; and it is therefore preferred to dissolve merely 75 to 80 per cent. of the copper by means of the final liquor, and the remainder by further leaching with dilute acids.

Precipitation of the Copper.—The precipitation of the copper is sometimes preceded by a special treatment for obtaining the silver, separately from the copper.

The precipitation of the copper is universally done by means of metallic iron. Gibb proposed precipitating the copper with hydrogen sulphide, but this method was later given up at the Bede Metal Works where it was tried on a large scale.

For precipitation with iron, the iron used was either, wrought scrap, or sponge iron reduced from the residues. Light scrap is better than heavy scrap, but the copper precipitated, owing to more impurities, gives a lower grade cement copper. The precipitation takes place in wooden tanks like those used in leaching the ore, and are furnished with a steam pipe for heating the copper liquor. The tanks are filled with scrap iron; copper liquor is run upon it and the steam turned on. The heating is continued till a bright strip of iron, held in the liquid, no

longer indicates the presence of copper in solution. At Oker, according to the degree of concentration of the liquors, the boiling takes place two or three times before all the copper is thrown down; the process lasts from one to three days, and requires as much iron as the weight of copper produced, which proves that a large part of the copper must have been in solution as cuprous chloride. Once a month the precipitated copper is removed from the tanks and washed. If sponge iron is used for precipitation of the copper, continuous stirring is required, for which at some works mechanical agitators are used, at others manual labor. At the Bede Metal Works an india-rubber hose, through which a blast of air passes, is moved about in the tank. Perfect mixture is thus obtained, and the precipitated copper contains only 1 per cent. metallic iron.

The composition of the copper precipitated by the various methods is shown by the following analyses by Gibb:

	Precipitated by		
	Sponge iron	Heavy scrap	Light scrap
	Per cent.	Per cent.	Per cent.
Copper	67.50	72.50	67.50
Arsenic	0.137	0.306	0.100
Silver	0.011	0.046	0.066
Lead	1.30	2.60	1.74
Ferric oxide	5.15	4.41	7.56
Carbon	5.10		
Silica	3.20		

At Oker the composition of the copper precipitated by scrap iron and dried at 100° C., was:

Cu,	77.45
Pb,	0.63
Ag,	0.10
Bi,	0.006
As,	0.04
Sb,	0.15
Fe_2O_3,	6.72
Al_2O_3,	0.99
Zn,	1.02
Mn,	0.02
Co-Ni,	0.03
CaO,	0.10
MgO-Alkalies,	2.71
SO_3,	4.58
Cl,	1.19
Insoluble in acids,	0.61
Oxygen-moisture (by loss),	3.654
	100.00

The copper precipitate from pyritic cinders made at the Witkowitz works, dried at 100° C., was composed as follows:

Cu,	11.30	=69.45 per cent. Cu
Cu_2O,	65.31	
Ag,	0.521	
Au,	trace	
Bi_2O_3,	0.19	
Fe_2O_3,	3.86	
ZnO,	0.45	
As_2O_3	1.18	
P_2O_5,	0.20	
$CuCl_2$,	0.32	
$FeCl_2$	0.16	
$CoCl_2$,	0.29	
$NiCl_2$,	0.07	
$AsCl_3$,	1.32	
$PbSO_4$	2.19	
Na_2SO_4	3.39	
$CaSO_4$,	5.32	
$MgSO_4$	0.59	
H_2O,	2.89	
	99.641	

The cement copper from the leaching works may be smelted to blister copper, or sent to the smelting works. The copper precipitated from aqueous solutions, if kept separate from that from the acid solutions, can be smelted direct to blister copper by adding to it lime and slags; the copper from the acid solutions is frequently so impure that it has to be mixed with raw ore, and smelted for "coarse metal" which yields blister copper only after second treatment. At some works both precipitates are melted together, being charged into the furnace while moist. The slag produced from this operation, containing from 3 to 10 per cent. copper, are charged into blast furnaces.

The furnace for smelting the copper precipitate used at English wet-extraction works are reverberatory furnaces of the well-known Swansea type. After smelting, the slag is skimmed off, and the copper tapped as blister copper. When sponge iron has been used, the excess of carbon prevents the copper from being melted directly into blister copper; therefore about one-half of the precipitate roasted in large furnaces similar to those used in roasting the ore. Here the carbon is burned off and the copper partly oxidized; the roasted precipitate is mixed with raw precipitate and smelted for blister copper. The blister copper is refined by roasting to oxidize the iron, sulphur, etc., followed by reducing with charcoal the oxide of copper produced in the roasting, and poling according to the method of smelting usually employed by the copper smelter. The copper produced in this way is pure and tough.

Precipitation of the Silver.—Most cupriferous pyrites contain some silver, and small quantities of gold. The cupriferous pyrites cinders from Spain, according to Phillips, contain on an average of 0.0027 per cent. silver, and 0.0001 per cent. gold. On roasting with salt, most of the silver and much of the gold is converted into the chlorides. Owing to the solubility of silver chloride in a solution of other chlorides, and the solubility of gold chloride in water, the silver and gold chlorides are extracted with the copper by the leaching solvent. At the present time, when copper is refined electrolytically at a small cost, no attempt is usually made to recover the gold and silver separate from the copper. In earlier years, however, this separation was desired, and various schemes were proposed for their separate recovery.

Claudit Process.—Of the methods proposed for the separate recovery of the silver and gold, that devised by Claudit was quite generally employed.

This process consists in precipitating with a soluble iodide the silver from the liquors in the state of AgI, silver iodide, which is quite insoluble in chloride solutions. Only the first liquors, rich in silver, are subjected to the Claudit process for the precipitation of the silver. The other solutions are returned to the ore, or they are too dilute in silver to make its recovery profitable. The liquors, from the leaching tanks, and before precipitating the copper, are run into settling tanks, where they are completely settled and their silver contents accurately estimated by adding to a certain volume of muriatic acid and a solution of lead acetate, and afterward potassium iodide. The precipitate is collected on a filter, washed, dried and fused with a flux of soda, borax and finely pulverized carbon. The lead regulus is cupelled, and from the weight of the silver thus obtained, that contained in the liquors in the settling tanks is computed. To the liquor in the settling tanks is then added a solution of potassium, sodium, or zinc iodide of known strength, so that the quantity is just sufficient to precipitate all the silver; the iodide solution is diluted to such an extent that it amounts to one-tenth the volume of the liquid.

The reactions for the precipitation of the silver with sodium and zinc iodides are:

$$AgCl + NaI = NaCl + AgI.$$
$$2AgCl + ZnI_2 = ZnCl_2 + 2AgI.$$

The precipitated iodide of silver is allowed to settle for about 48 hours, and tested in the laboratory to see if the precipitation has been complete. The liquors are then run into the copper precipitating tanks, where they are treated in the usual way for the precipitation of the copper.

The quantity of iodide employed for the precipitation is much larger than that corresponding to the silver present, since a portion of the lead is also thrown down as $PbCl_2$. The silver is probably precipitated before the lead, but a fractional precipitation is not possible, so that necessarily a corresponding excess of the precipitant is required.

The precipitate, consisting principally of AgI, PbI_2 and $PbSO_4$(which is deposited on cooling the liquor), is well washed with water; and after a sufficient quantity of it has been collected, it is treated with metallic zinc and hydrochloric acid or with sodium sulphide;

$$2AgI + Zn = ZnI_2 + 2Ag. \text{ or}$$
$$2AgI + Na_2S = 2NaI + Ag_2S.$$

Thus the AgI and PbI_2 are decomposed completely, the $PbSO_4$ partly, and liquor containing zinc or sodium iodide is obtained, which is employed again and the cycle continued indefinitely.

After two or three days the precipitated liquor is drawn off, and run into copper precipitating tanks where the copper is precipitated, in the usual way. The liquors may still contain 2 to 3 milligrm. of silver per liter. The tanks are furnished with two outlets, one at the bottom and the other about 8 inches higher. The desilverized solution is drawn off the upper hole while the precipitate remains undisturbed on the bottom. New liquor from the leaching vats is then let in and the procedure repeated until there is a sufficient silver slime in the bottom that it has to be recovered. This is usually done every month or two, depending on the percentage of silver in the ore.

The precipitate obtained, treated with zinc and hydrochloric acid, ready for melting, contains from 3 to 10 per cent. silver and usually some gold. An anlaysis shows the following composition:

Ag,	5.95
Au,	0.06
Pb,	62.28
Cu,	0.60
ZnO,	15.46
Fe_2O_3	1.50
CaO,	1.10
SO_3,	7.68
Insoluble,	1.75
Oxygen and loss,	3.62
	100.00

About two-thirds of the silver and gold originally contained in the roasted ore is recovered, with care, by the Claudit method. Under

normal conditions, from 10 to 15 per cent. of the iodide is lost in precipitating the silver.

Disposition of the Residues.—The residues, from the leaching, make a valuable ore of iron, and is known as "purple ore" or "blue billy." In this way the additional profit may be realized. The following is the composition of two average samples:

Ferric oxide,	90.61	95.10
Copper,	0.15	0.18
Sulphur,	0.08	0.07
Phosphorous,		
Lead sulphate,	1.46	1.29
Calcium sulphate,	0.37	0.29
Sodium sulphate,	0.27	
Sodium chloride,	0.28	
Insoluble,	6.30	2.13
	99.62	99.55
Metalic iron	63.42	66.57

This shows an excellent quality of iron ore, entirely free from phosphorus, and containing but little sulphur. Its slight percentage of copper does no harm. The lead contained in the pyrites remains behind in the residue in the shape of sulphate, and injures its quality as an iron ore. Schaffner proposed drenching the residues with a solution of calcium chloride, heated to about 40° C., and acidulated with hydrochloric acid. By mutual decomposition, gypsum and lead chloride are at once formed, which remains dissolved in the acid liquor. This is run off and brought in contact with metallic iron, which precipitates the lead in the metallic state. After washing, the purple ore is quite free from lead sulphate. At the same time the $CaCl_2$ dissolves the last traces of copper and silver present as Cu_2Cl_2 and $AgCl$; these are precipitated along with the lead. It should be noted that hydrogen sulphide fails to indicate the lead in a solution of calcium chloride acidulated with hydrochloric acid.

The only drawback to the use of pyritic residues in smelting for iron is their fineness, which militates against their desirability. Unsuccessful attempts for a long time were made to agglomerate this ore but without success. At present, however, this is cheaply done by sintering, or by partially fusing it. It can cheaply be sintered by mixing with it from 7 to 10 per cent. coal or coke dust, the mixture moistened to the proper consistency, placing it on a permeable hearth such as broken limestone, and then applying suction (down draft) so that the intense ignition of the coal dust fuses the ore and agglomerates it into a strong porous mass, and puts it in ideal condition for smelting.[1]

[1] John E. Greenawalt, U. S. Patent, 839,064, Dec. 18, 1906.

Experiments made in Denver by this method gave excellent results both as to cost of sintering and product obtained. These experiments have since been duplicated in large installations in working plants.

In some works the residues are briquetted, and the briquetts, after being dried, are subjected to a high temperature, so that by partial fusion, they become coherent. In still other works the residue is sintered and nodulized by passing the purple ore through a rotary cylinder similar to those used in revolving roasters, in which the ore is heated to a high temperature by means of powdered coal blown in at the discharge end. This product varies in size from that of rice to that of walnuts, and forms hard balls more or less thoroughly sintered. By the Gröndal method the cinder is formed into briquetts of uniform size by an automatic plunger press. The briquetts are loaded on flat cars, which are then slowly pushed through a channel furnace 150 to 200 ft. long, where they are gradually heated until they arrive at a zone of the furnace where the temperature reaches 2400° F. The finished product is hard and strong, but porous, so that it is well suited to blast furnace work and open hearth practice.

The cost for nodulizing or briquetting will vary from $0.75 to $1.25 per ton. Costs for sintering have not yet been established.

Longmaid-Henderson Process at the Helsingborg Copper Works, Sweden.—In preparing the tanks for the ore, standard bricks are placed on edge on the bottom. On these special perforated brick, 12 in. square, are laid as a false bottom for a filter composed of straw or screened lump cinder, iron ore or something similar, on top of which the ore is charged and leveled. The tanks are built elliptical in shape, one diameter of which is 10 ft. and the other 6 ft. The inside depth is 4 ft. and the thickness of stave 5 in.

After leveling the charge, acid liquors of 5 to 8° B. strength, obtained in previous leaching, are let into the tanks. The ore is still warm from the roasting. The first liquor issuing from the vats is very strong—40° B. It contains about 5 per cent. copper and nearly all the silver. It is transferred immediately to the silver precipitation department.

When the strength of the liquor as it is drawn from the vats has gone down to 22° B., it is taken to the copper precipitators. This continues until the strength of the outgoing liquor has gone down to 10° B. The incoming liquor is shut off and in its place acid from the towers is let into the tank. The acid is allowed to remain in the tanks two hours, at the end of which time the liquor is exchanged for fresh acid, which in its turn remains two hours. The liquor so obtained is used in the first application for freshly filled tanks.

After this leaching, the ore is washed with water, first with wash water from a previous operation and finally with fresh water. To test whether

all the copper is extracted, a well-polished iron plate is immersed in the off coming solution; if there is no coloring of copper, the leaching is finished.

The wash water ought to have a temperature of about 50° C. The time of leaching is usually about 40 hours for a 10-ton charge.

Of the copper in the roasted ore about 80 per cent. is soluble in warm water,

16 per cent. soluble in weak hydrochloric acid,

4 per cent. insoluble, and remains in the purple ore.

The purple ore is briquetted and sintered and then smelted for iron. The crude purple ore contains 60.6 per cent. iron and 0.17 per cent. sulphur; the fused briquetts contain 60.6 per cent. iron and 0.023 per cent. sulphur.

Longmaid-Henderson Process as Carried out at the Works of the Pennsylvania Salt Manufacturing Co., Natrona, Pa.—A description of a large modern plant, treating approximately 200 tons of pyritic cinders a day by the Longmaid-Henderson process is given by Joel G. Clemer.[1] The method of operation is as follows:

The pyritic cinders are ground dry in Chillean mills, to about 20 mesh, and mixed during the operation with 10 per cent. salt, testing high in NaCl. The mixture is then lifted by bucket elevators to overhead hoppers from which it is drawn into tram cars, weighed, and dumped into the furnace hoppers, or pipes set into the floor over the furnaces. Should the unburnt sulphur in the cinders not be equal to the copper, sufficient unroasted ore is added in the mill to bring it up to 1.5 times the copper content.

Then 9600 lb. of mixture is taken as a furnace charge, and is heated to a very dull-red heat, say 800° F., and well stirred. When properly worked such a change will be finished in about 8 hours making three charges every 24 hours per furnace. The charge, when finished, is drawn from the furnace to the floor to cool, and then transported in tram cars to the leaching vats.

Muffle furnaces have almost entirely superseded the old reverberatory furnaces for chloridizing roasting. Contrasting the action of the two types of furnaces, the muffle possesses the advantage of requiring but one-half the condensing capacity, as only the gases resulting from the chloridization pass through the towers while in the reverberatory the gases of combustion as well must pass through. Apart from this decided advantage of the muffle furnace, better results are obtained, as both the gases from the reaction and those from the combustion are under separate control.

The construction of the modern muffle furnace is well illustrated in detail in Fig. 49. The arch at the fire-box is made double to prevent the

[1] Min. Industry, Vols. VIII and IX.

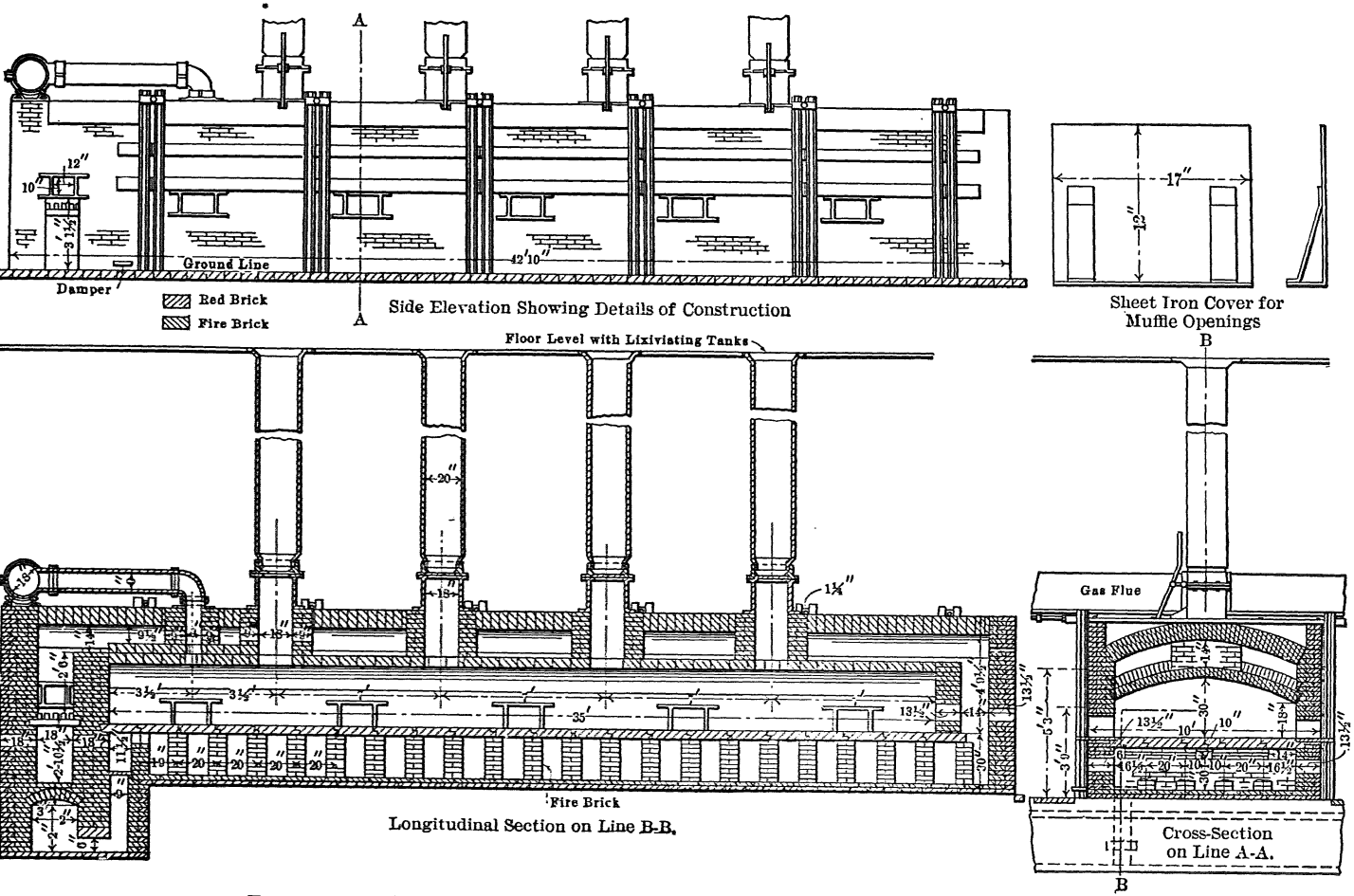


FIG. 49.—Hand muffle furnace for chloridizing roasting of cupriferous pyrites cinders.

cinders from becoming overheated at that end, and the fire flue is placed beneath the furnace rather than at the end of the passageway, which is constantly traversed by the workmen. A bridge wall is constructed beneath the bed of the hearth of the muffle and guides the heat directly beneath it to the entrance of the underground flue at the fire-box end where the fire flue damper for controling the draft is located. The furnace has doors on both sides of the fire and muffle. The furnace shown in the illustration was designed for the treatment of cinders containing less than 2 per cent. copper, with a normal amount of sulphur, the charge being of usual weight. The hoppers hold sufficient material for an entire charge.

In the construction of the tanks every supporting timber, plank, and pin should be painted on all sides with hot soft tar before being put

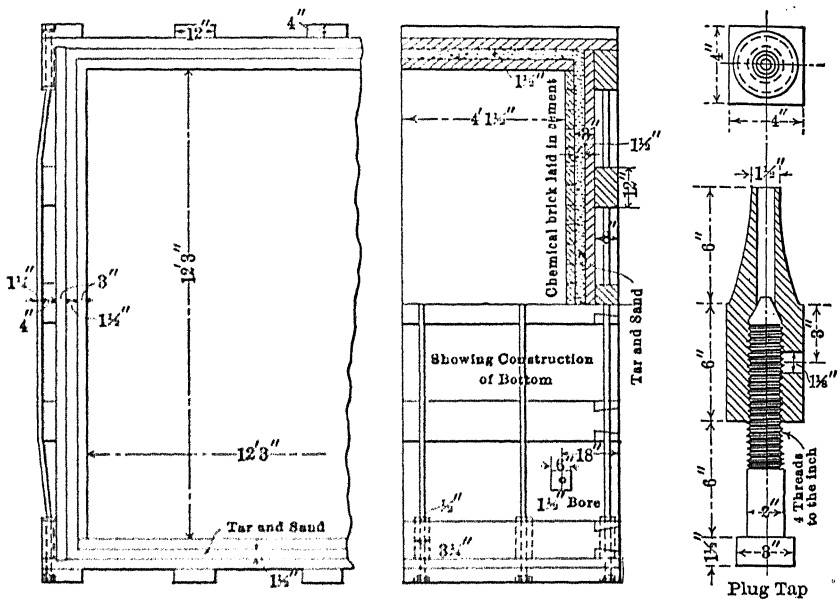


Fig. 50.—Details of tank construction for leaching cupriferous pyrites cinders.

in place. This is absorbed by the wood and protects it against the destructive action of the acid liquors. The tanks should be constructed of 3-in. plank, with an inside shell of the same thickness, and a space of 3 in. between the plank and the shell. All should be put together with wooden pins and bound together as shown in the accompanying drawing, Fig. 50. The space between the tanks and shells should be filled with a mixture of hard tar and sand. The bottom should be covered to the depth of 3 in. with the mixture fused to that between the shell and tank. This bottom covering should be protected against wear of shovels by a layer of chemical brick laid in cement.

The holes for drawing off the liquor are bored through wooden blocks 6×6 in. square set inside of the tank near the bottom, and provided with wooden spigots or plugs, extending to the weak and strong liquor launders. All the launders are made preferably of very sappy yellow pine, dug out, with the ends or joints halved together and caulked with oakum and red lead.

The proper dimensions for the leaching, settling, and precipitating tanks are, 12×12×4 ft.; 12×12×6 ft., and 12×12×6 ft., respectively.

In preparing the mixture of hard tar and sand, composed of about equal parts, care must be exercised not only to produce a homogeneous mass, but also that all the moisture and air be expelled. The usual method of procedure is to heat the hard tar in a large kettle, and stir it until the moisture and air have been expelled, then adding the sand hot and stirring the mixture until the desired result is obtained. The sand must of course be first screened, and have all combustible matter burned out of it before mixing with the tar.

The bottom of the leaching tanks are provided with hard-burned red brick laid flat side by side, and covered with old hay or small pieces of refuse coke. This makes a quite durable filter.

The roasted mixture, charged into the tanks, is first leached with weak liquor from a previous operation, and then with water and dilute hydrochloric acid from the condensing towers connected with the furnaces. After leaching is completed the residue (purple ore or blue billy) is shoveled directly into gondola cars for shipment to the iron smelters.

All the copper liquors are run into settling and storage tanks; the weak liquor being pumped or blown back with steam injectors, to the leaching tanks when required. Any liquors of 18° B. and upward are left in the settling tanks until all the lead sulphate, etc., has settled out. The lead sulphate usually contains some gold; indeed an average of $100 per month is not an unusual recovery in a plant of the capacity described, and it is therefore essential for the recovery of this as well as for other reasons that everything that will settle out of the liquor, be given time to settle in three tanks. A part of these tanks may also be used for precipitating the silver with the iodide, in Claudit's process, but since in practice this process leaves an average of 5 oz. silver in a ton of precipitated copper, and since electrolytic copper works, as well as blue vitriol works, handling or using silver- and gold-bearing copper, will pay for at least 95 per cent. of the silver content and full market value of the copper and gold contents of the cement copper, this part of the copper extraction does not pay, especially since the cost per annum of precipitating the silver by the iodide method in a plant of this size is not less than $12,000.

After the lead sulphate, etc. has settled out of the strong liquors, they are run into the copper tanks and the copper, silver, and gold con-

tents are precipitated by means of clean thin scrap iron from the rolling mills. These tanks should have wooden slats so placed as to form an open false bottom about two feet above the real bottom, for the support of the scrap iron. Live steam is let into the liquor during the process of precipitation. The steam serves to accelerate the process, and also keeps the liquor in motion, and washes off the copper from the iron as fast as it is precipitated. The copper naturally finds its way between the slats to the bottom of the tank, and when it is desirable to remove it, the remaining scrap iron can readily be removed from the false bottom practically free from copper. The cement copper, on the bottom of the tank, after washing through perforated cast-iron plates set in a frame over the tanks, assays about 90 per cent. Cu; 35 oz. Ag. and 0.15 oz. Au, per ton. The precipitated chloride solutions are then run into the sewer, by first passing it through a series of tanks in the ground, which are filled with scrap iron, to recover any copper and silver which may have been left in the waste chloride solutions and the wash waters.

The cost of treating Spanish pyrites cinders, as above described, at Natrona, Pa., in a works having a daily capacity of say 200 tons of mixture (cinder and salt) will be about as follows:

2 samplers,	at $2.50	$5.00
6 mill men,	at 1.75	10.50
1 mechanic,	at 2.00	2.00
2 engineers,	at 2.00	4.00
3 firemen,	at 1.75	5.25
4 weightmen and furnace chargers,	at 1.75	7.00
28 furnace men,	at 1.75	49.00
1 hoistman,	at 2.00	2.00
27 furnace material handlers, coal, and cinder wheelers,	at 1.50	40.50
2 leachers,	at 1.75	3.50
4 copper precipitators,	at 1.50	6.00
Unloading cinders and salt,		20.00
Loading purple ore for shipment,		15.00
21 tons of salt,	at 3.00	63.00
Pyrites fines,		7.00
20 tons of coal,	at 1.00	20.00
5 1/2 tons of sheet-iron scrap,	at 9.00	38.50
Repairs, depreciation, management, etc.		40.00
		$338.25

Or $1.87 per ton of 2000 lb. pyritic cinders, or $1.69 per ton of 2000 lb. of mixture.

Cost of Producing Copper by the Longmaid-Henderson Process in a Modern Plant, Using Mechanical Roasters.—The cost, per pound of copper extracted, in a modern Longmaid-Henderson process plant

located in the Eastern United States, using mechanical furnaces, and treating from 300 to 400 tons of pyritic cinders per day having a copper content of 2.27 per cent., and a sulphur content of 2.28 per cent., is as follows:

COST, PER POUND OF COPPER EXTRACTED IN MODERN LONGMAID-HENDERSON PLANT

Items of expense,	Per pound of copper
Process labor,	$0.0136
Misc. supplies,	0.0010
Coal,	0.0027
Fuel oil,	0.0067
Salt,	0.0166
Scrap iron,	0.0018
Repairs, all labor and material,	0.0095
Total,	$0.0519

The tailings are worked up by agglomeration into an iron ore of the following composition:

Metallic iron,	68.00 per cent.
Sulphur,	0.07 per cent.
Copper,	0.15 per cent.
Silica	3.00 per cent.
Phosphorous,	0.012 per cent.
Oxygen, etc.,	28.77 per cent.

In the Western United States, under somewhat similar conditions, in treating material having a copper content of 2.27 per cent., the estimated cost per ton of 2000 lb. is as follows:

Items of expense,	Cost per ton of ore
Process labor,	$0.71
Misc. material,	0.07
Coal,	0.21
Lubricating oil,	0.01
Fuel oil,	0.37
Salt,	0.99
Scrap iron,	0.15
Repairs, labor and material,	0.45
Total,	$2.96

Elimination of Arsenic, Antimony and Bismuth.[1]—In the Longmaid-Henderson process the chloridization of the copper preparatory to its solution, is accompanied by the three elements, arsenic, antimony, and bismuth. These chlorides being volatile at low temperatures are carried off to a greater or less extent, and are largely dissolved in the wash water and collected with the condensed acids, in the tower liquors. The aresnic

[1] Trans. A. I. M. E., Vol. XXXIII, p. 667, Allen Gibb.

in a notable quantity and the antimony in a less amount mainly in combination as arsenates and antimonates, with some bismuth remain in the roasted ore. In washing with water, these salts, as well as the bismuth that remains in the roasted ore, are dissolved only in minute traces, so that if the copper is precipitated from these solutions it would be practically free from impurities. The copper, insoluble in water, that is in the roasted ore, is removed by the use of tower liquors, and under the action of this solvent a considerable proportion of the arsenic, antimony, and bismuth that remain in the calcined ore is dissolved. This increases the proportion of these elements that is already present in the tower liquors.

In the tower liquors, obtained by washing the gases from the furnaces, there was found: arsenic, 0.0222 gm. antimony, 0.0005 gm.; and bismuth, 0.0046 gm. per liter.

The proportion of impurities in the copper from the same ore vary greatly according to whether the practice of treating the aqueous and acid solutions separately is followed or not.

The following data is taken from practice in which the two solutions were not kept separate:

	Roasted ore		Precipitate		Total per cent. of elimination
	Per cent. actual	Per cent. relative Cu = 100 per cent.	Per cent. actual	Per cent. relative Cu = 100 per cent.	
Copper.....	4.65	100.0	73.33	100.0	
Arsenic.....	0.16	3.44	0.974	1.33	61.3
Antimony....	0.026	0.559	0.008	0.011	98.0
Bismuth.....	0.018	0.388	0.053	0.072	81.4

Extraction of Copper from Atacamite.[1]—At Chiquicamata, Chile, a multitude of small fissures, filled with atacamite, or oxychloride of copper, traverse the country rock, consisting of granites, pegmatites, syenites, in every direction. This kind of deposit, which appears to be in the nature of a stock work, a leaching process is usually adopted in order to extract the metal from the oxychloride.

In treating Atacamite ores the difficulty has been in the filtration of the liquid containing the dissolved copper. The chemical reactions which take place between the perchloride and oxide of iron on the one part and the ferric solution and argilaceous portion of the gangue on the other, result in the formation of a gelatinous precipitate, which has to be washed many times in order to get out the dissolved metal.

[1] *London Mining Journal*, June 30, 1906, Nicanor Argandona.

The first part in the treatment of the ore by a new process consists in converting, by the action of steam, a portion of the chloride of copper in the ore into hydrochloric acid and black oxide of copper, according to the equation:

$$CuCl_2 + H_2O = CuO + 2HCl.$$

A certain portion of the ore is put into large clay retorts, or into iron retorts lined with a thin coating of clay, and exposed at a temperature of 230° C., to the action of steam. Theoretically, there is sufficient water of combination in the ore itself to supply the quantity of vapor needed. The expenditure of steam is very small, but a certain quantity is necessary in order to accelerate the reaction. The black oxide resulting from this process is reduced by smelting.

The second part of the process consists in submitting the ore, which contains from 3 to 4 per cent. copper, to the action of hydrochloric acid obtained as above described. For this purpose cylindrical wooden or brick vats are used, having special lining of pitch. Ordinary filters can be employed in this operation, as no gelatinous precipitate is produced.

CHAPTER XI

COPPER PRECIPITANTS

Iron.—Iron is almost universally used in the chemical precipitation of copper from its solutions. It presents many advantages over other precipitants; it is usually quite cheap, generally obtainable, and gives the resultant copper in the metallic condition. Scrap iron is ordinarily employed, but scrap iron, while cheap enough in industrial centers becomes prohibitive in mining districts which are located long distances from railroads and from the source of iron supply.

For the precipitation of copper by iron, the solution should be as free as possible from acid or ferric salts. The acid and ferric salts act on the iron and waste it without precipitating any copper. Theoretically 88.8 lb. of iron are required by weight to precipitate 100 lb. of copper from sulphate solutions. In practice, the consumption greatly exceeds the theoretical amount, because the solution cannot be kept free from acid or ferric salts and because scrap iron which is contaminated more or less with impurities, not available for precipitation is ordinarily used. With care, the consumption of iron in precipitating copper from sulphate solutions, in practice, will average about 1.5 lb. of iron per pound of copper precipitated; under the adverse conditions of free acid, ferric salts, and impure scrap iron, the consumption of iron may rise to 2 or even 3 parts of iron to 1 part of copper.

Ferrous sulphate by prolonged contact with air is decomposed into free sulphuric acid and ferric sulphate; the former dissolves iron, and the latter combines with it to again form ferrous sulphate. The following equations explain the principal chemical changes that take place, in precipitating with iron from a sulphate solution.

$$(1) \quad CuSO_4 + Fe = Cu + FeSO_4.$$

This represents the theoretical reaction, without any interfering elements, and if it could be theoretically carried out, only 88.8 parts of iron would be required to precipitate 100 parts of copper. As both ferric sulphate and free sulphuric acid are likely to be in the solutions, the following reactions also take place:

$$(2) \quad Fe_2(SO_4)_3 + Fe = 3FeSO_4.$$
$$(3) \quad H_2SO_4 + Fe = FeSO_4 + 2H.$$

The excess of iron consumed may be said in general to be due to the quantity of ferric iron and free acid in the copper solution. The tendency

of the iron is to reduce the ferric to the ferrous salts, when the theoretical amount will be more nearly approached.

Some of the ferric sulphate may not be directly reduced by the iron, but may act on the precipitated copper, as shown by the following equation:

$$Fe_2(SO_4)_3 + Cu = CuSO_4 + 2FeSO_4,$$

but as the copper so dissolved has to be precipitated at the expense of the iron, the ultimate amount of iron consumed in reducing the ferric salts is the same.

An accurate determination of the iron consumed per ton of copper produced can be arrived at by testing the ingoing and outgoing solutions to the precipitators, to determine the amount of the copper precipitated, of the ferric iron reduced, and of free sulphuric acid neutralized, and calculating the quantity of metallic iron required to bring about these changes. S. R. Adcock[1] gives the following partial analysis and calculations, of samples of liquor entering and leaving one of the cementation tanks at Rio Tinto.

ANALYSIS OF LIQUOR ENTERING AND LEAVING TANKS, IN GRAMS PER CUBIC METER

	Entering	Leaving
Copper	2.064	3
Ferric iron	1.328	Nil
Sulphuric acid	1.198	712

CALCULATIONS IN GRAMS PER CUBIC METER OF LIQUOR

Cu precipitated,	$2.064-3=2.061\times 8/9=$	1.832 grm. of iron required.
Ferric iron reduced,	$1.328\times 1/2=$	644 grm. of iron required.
Sulphuric acid neutralized,	$1.189-712=486\times 4/7=$	278 grm. of iron required.
Total iron,		2.774 grm.

2.061 grm. of copper precipitated would require 2.774 grm. of iron or one part of copper precipitated from the liquor would require 1.345 parts of iron. Taking the metallic contents of the pig iron used at 92 per cent. the consumption in this instance works out at 1 part of copper to 1.462 parts of pig iron. In addition, there is a small consumption of iron, due to impurities in the solution and waste in cleaning up the copper."

It is desirable, for the best work in precipitation, to have the copper solution slightly acid. A slight acidity tends to hasten the precipitation, and prevents the separation of basic iron salts. In general, the acid con-

[1] Min. Ind., Vol. IX, p. 238.

tent of the copper solution for precipitation in a running stream, or if agitated, should not be more than 0.1 to 0.2 per cent. If the acid much exceeds this amount the consumption of iron is likely to be correspondingly high.

Every precaution should be taken to reduce the ferric iron to the ferrous condition before precipitating the copper, for in most instances the excessive consumption of iron during precipitation, can be traced to the high ferric iron content of the liquor under treatment.

If there is arsenic in the ore it is likely to go into solution with the copper, and is to a certain extent precipitated with it. When the liquor is rich in copper and the precipitation is taking place rapidly, the amount of arsenic precipitated is comparatively small, but as the liquor gets weaker in copper, the proportion of arsenic to copper precipitated is much higher.

If the copper is dissolved as a chloride, either by hydrochloric acid or metal chloride, the precipitation may take place either from the cupric or cuprous chloride, as shown by the following reactions:

$$CuCl_2 + Fe = FeCl_2 + Cu.$$
$$Cu_2Cl_2 + Fe = FeCl_2 + 2Cu.$$

It is evident, therefore, from these equations, that twice as much copper is precipitated, theoretically, per unit of iron from cuprous chloride as from cupric chloride. The precipitation from the cupric chloride is theoretically the same as that of cupric sulphate—88.8 parts of iron are required to precipitate 100 parts of copper—whereas only 44.4 parts of iron are required to precipitate 100 parts of copper from cuprous chloride.

In practice, at Stadtberg, 127 parts by weight of iron were required to precipitate 100 parts of copper from a chloride solution in which hydrochloric acid was used as the solvent. In the Hunt and Douglas process, in which the copper is precipitated from cuprous chloride, only from 50 to 70 parts of iron are required to precipitate 100 parts of copper.

If there is free hydrochloric acid or ferric chloride in the solution, iron will combine with them to form ferrous chloride, and will consequently be wasted, as in the analogous procedure in the sulphate solution; this may be shown by the following equations:

$$2HCl + Fe = FeCl_2 + 2H.$$
$$2FeCl_3 + Fe = 3FeCl_2.$$

The neutralization of the free acid, and the reduction of the ferric to the ferrous chloride, is quiet as necessary as with sulphate solutions to effect the best economy in the precipitation.

The iron for precipitation, whether from a sulphate or chloride solution may be used in the form of wrought, pig iron, iron bars, or iron spong.

Pulverent iron in the form of ground sponge acts most rapidly. Bar iron yields a coarse grained cement copper, with but little coherence; gray pig iron, which acts faster than white iron, gives a more pulverent precipitate, while white iron throws down coherent masses. The graphite in the pig iron separates out during the precipitation and renders the cement copper impure.

Sponge Iron.—It is evident that if iron is used as the precipitant of copper, it would be quite an advantage if the iron could in some way be cheaply manufactured at the copper reduction works. The purchase of scrap or pig iron, and its transportation to the reduction works at the mines, is usually a prohibitive expense. An ordinary iron smelting plant could not be considered.

The manufacture of sponge iron, in which a high-grade ore is reduced to metal without the necessity of smelting or fluxing, has in a measure solved the problem, but notwithstanding that the manufacture of sponge iron and its application to copper precipitation has long been known, its use has not met with much encouragement.

The principle of the manufacture of sponge iron is quite simple. If ferric oxide, Fe_2O_3, is heated in a highly reducing atmosphere, the oxygen of the iron oxide combines with the reducing gases, and the resultant product is finely divided metallic iron, containing more or less impurities. Great care must be used in cooling the iron to prevent reoxidation, so that the cooling, as well as the heating must be done in the presence of reducing gases.

The following description by Lunge[1] gives the details of early European practice and its application to copper precipitation.

"The precipitation of copper from its solutions by means of iron takes place more rapidly by employing spongy iron, as was done at the Bede Metal Works. This product is made by reducing ferric oxide at so low a temperature that the iron cannot combine with the carbon and cannot melt, but remains in the finely divided state as 'sponge.' This method was tried in England for the first time in 1837. Gossage, in 1859, was the first to use it in the wet method of copper extraction.

"The furnace usually employed in making sponge iron, is a reverberatory in which the flame, after having passed directly over the charge, returns below the furnace bed, and thus heats the charge indirectly from below. Figs. 51 and 52 show the essential details of the furnace. It is, in the drawing, 28 ft. 9 in. long; the working bed has a length of 22 ft. and a width of 8 ft. Dwarf walls, *a a*, 9 in. high, divide it into three compartments, which on one side have two working doors, *b b*, each. Each compartment is charged and finished by itself. The working doors are of cast metal and run in air-tight frames; the same is the case with the fire doors. The fireplace is constructed for generating a reducing flame; the grate has a surface 4×3 ft.; and the bearers *d*, are 3 ft., latterly even 4 ft. 8 in.

[1] "Sulphuric Acid and Alkali Manufacture," p. 815.

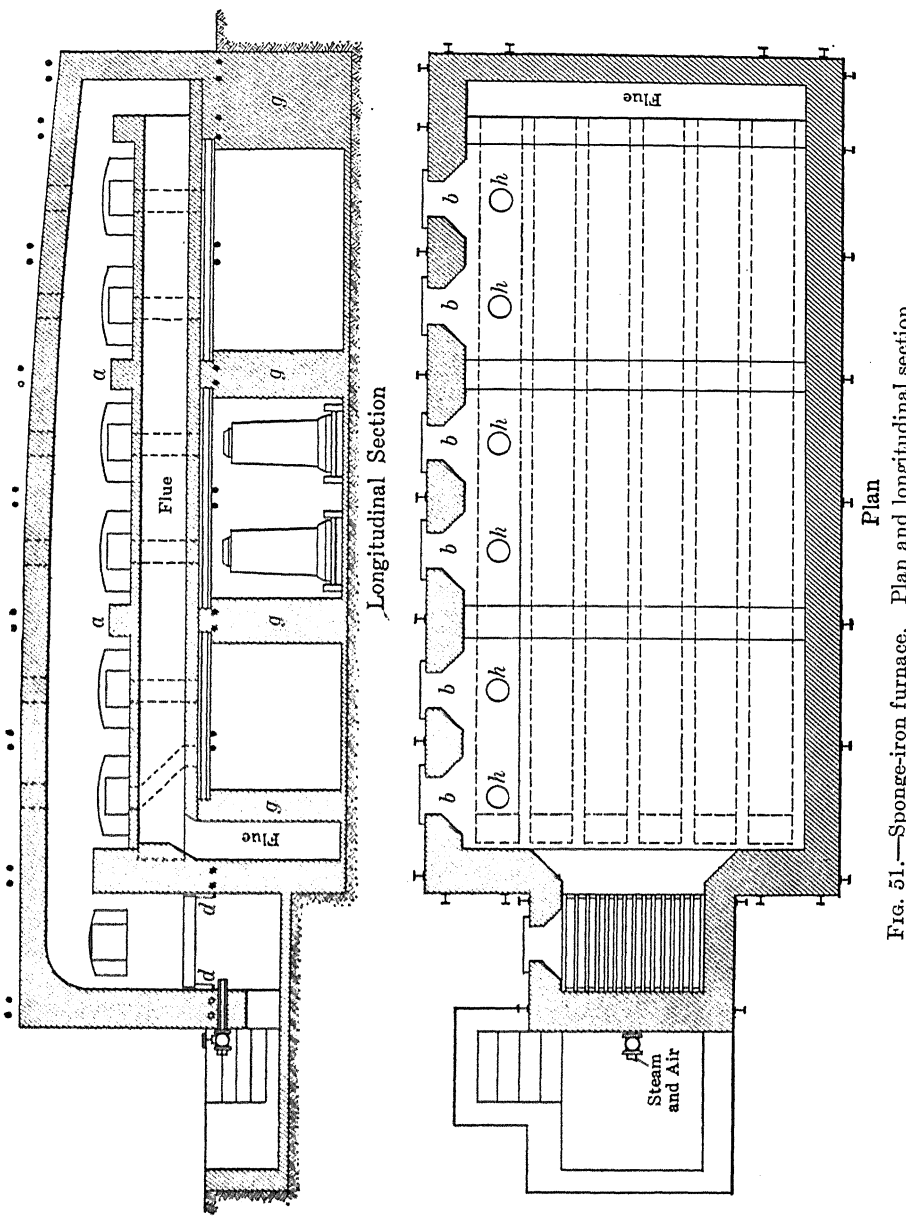


FIG. 51.—Sponge-iron furnace. Plan and longitudinal section.

below the fire bridge; so that a very deep layer of fuel is obtained, which does not allow any oxygen to get inside the furnace. The furnace bed is formed by fire tiles 4 in. thick, with rabbited edges, partly resting upon the walls forming the divisions of the lower flues, partly upon railway-bars.

"The flame having traveled through these flues, descends in a vertical shaft along the fire bridge, and thence goes to the chimney. In this descending shaft there is a fireclay damper, which is closed every time before a working door or fire door is opened. The 9-in. furnace roof is surmounted by a flat cast-iron dish, supported by short pillars, for drying the ore and mixing it with coal; the mixture is charged into the furnace through the 6-in. pipes, *f*, carried through

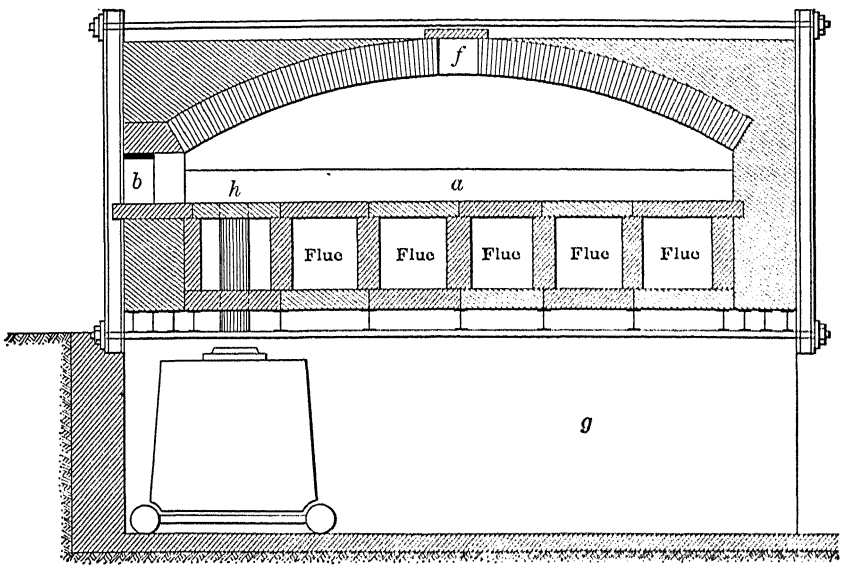


FIG. 52.—Sponge-iron furnace. Transverse section.

the arch. The whole furnace rests on brick pillars, *g*, and the floor on the working sides must be so much higher than that on the discharge side, that the discharging boxes can be run underneath the furnace between the brick pillars. The discharging takes place through 6-in. pipes, *h*, descending in front of the working doors through the furnace bottom and the lower flues.

"The discharge boxes are made of sheet iron, of rectangular section, tapering toward the top. The cover is fast, and has in its center a 6-in. opening with upright flange, by which the box is connected with the discharge tube. The bottom of the box is movable, and turns on one side on hinges, while the other side is fastened by bolts and cotters. The whole is mounted on four wheels in such a way that they do not interfere with the movements of the bottom. Each box has a capacity of 12 cu. ft.

"When the furnace is at a bright red heat, it can be charged. Each compartment receives a charge of 2000 lb. of 'purple ore' and 600 lb. of coal, which have passed through a sieve with eight holes to the lineal inch.

"The charging takes place from the cast-iron dish above the furnace roof.

The fire and working doors are closed, so that the air enters solely through the coals on the grate, care being taken that the burning mass does not become hollow, lest uncombined oxygen should get inside the furnace. The time of reduction in the compartment nearest the fire bridge varies from 9 to 12 hours; in the second it is about 18 hours, and in the third about 24 hours. The depth of the charge lying on the bed is about 6 in. During the time of reduction each compartment must be turned over twice, or even three times. Although during this time the damper is closed, a little air always enters the furnace; but the turning over is indispensable, as the mass would otherwise cake together. The time above stated refers to a bright red heat; a low heat is sufficient for reduction and the iron thus made is even better for the precipitation of copper; but as in this case much more time is required for reduction (up to 60 hours) this style of working does not pay. The fire place being so deep, fresh coal need only be thrown on twice or three times every 12 hours, say 1500 lb. per ton of ore.

"The completion of the reduction is ascertained by testing. A small sample is taken out, put on an iron plate, covered with a brick until it has become cold, and 1 grm. of the (unoxidized) central part tested by a cupric sulphate solution of known strength, which is run from a burette on the spongy iron with frequent stirring; from time to time a drop is put on a bright blade of iron, to see whether any stain of copper is produced upon it. When the reaction in any of the three compartments is finished, the damper is closed; two of the discharging boxes are run underneath the furnace, and their openings connected with the discharge pipes by an iron hoop luted with clay; then the charge is raked down into the boxes as quickly as possible. The boxes are then closed with the loose cover, run out again, and allowed to cool for 48 hours. They are then lifted by a crane, and the cotters are knocked; whereupon the bottom turns on its hinges and the whole mass of spongy iron readily falls out, owing to the box tapering upward. The sponge is then finely ground in a heavy chilean mill 6 ft. in diameter, and passed through a sieve with fifty holes per lineal inch. It is now ready for the precipitation of the copper.

The following is an analysis of sponge iron produced from purple ore, from Spanish pyrites.

	Purple Ore	Sponge Iron
Ferric oxide,	95.10 per cent.	8.15 per cent.
Ferrous oxide,		2.40 per cent.
Metallic iron,		70.40 per cent.
Copper,	0.18 per cent.	0.24 per cent.
Lead oxide,	0.96 per cent.	
Lead,		0.27 per cent.
Sulphur,	0.07 per cent.	0.07 per cent.
Calcium oxide,	0.20 per cent.	
Sodium oxide,	0.13 per cent.	
Sulphur trioxide,	0.78 per cent.	
Alumina,		0.19 per cent.
Zinc		0.30 per cent.
Silicious residue,	2.13 per cent.	9.00 per cent.
	99.55 per cent.	99.62 per cent.

"When spongy iron is employed for the precipitation of copper, continuous stirring is required, for which at some works a mechanical agitator is used, at others, manual labor."

Any good iron ore may be converted into iron sponge, or the concentrate residues, after roasting and copper extraction.

Crucible Method of Iron Ore Reduction.—Another method of reducing iron ore in connection with copper precipitation—that in which the mixture of ore and coal is reduced in a crucible—might be considered. This method of manufacturing iron has been in use in China from remote antiquity, and large quantities are in this way reduced there.

At Shansi, China, the crucibles are about 19 in. high and 6.5 in. in diameter. They are filled with a mixture of ore which has been broken and sorted to walnut size; coal of about the same size, and coal dirt. The proportions are four baskets of ore, one basket of coal, and one basket of coal dirt on top. The crucibles are heated in a stall furnace. It takes about 16 hours to reduce the iron. After cooling the crucibles are removed and broken and the iron taken out.

Precipitation with a Coke-iron Couple.—W. L. Austin[1] gives the result of a 30-day comparative test on a working scale, using ordinary mine waters, between iron and the coke-iron couple as the precipitant. The average daily assays showed the following extraction effected within 8 ft. from where the waters entered the precipitation boxes:

Percentage of copper removed in the boxes containing clean wrought iron	.25
Percentage of copper removed in the boxes containing coke-iron couple	.43

It was found that when coke was added to the iron in the precipitating boxes through which the sulphate mine waters were flowing, by actual weight from 1.15 to 2.66 lb. copper was precipitated to the pound of iron consumed. One of the advantages in employing the coke-iron couple in cementation is that the precipitation of the copper takes place within a short distance from the point where the liquors enter the boxes, thereby avoiding to a great extent the formation of basic iron salts which usually debase the cement copper.

Precipitation with a Copper-iron Couple.—If iron plates or a bundle of scrap iron in a crate are immersed in a copper sulphate solution and connected electrically with a copper plate to serve as a cathode, no copper is precipitated on the iron, but all is precipitated on the copper plate. The iron acts as a soluble anode, going into solution as ferrous sulphate, while the copper is deposited in a dense, practically pure condition on the copper sheet. In this case the iron and copper act as a battery, with a theoretical difference of potential of 0.81 volt. If more rapid precipita-

[1] "Mines and Methods," January, 1911.

tion is desired than given by this action alone, a current from a dynamo may also be used in connection with that produced by the iron and copper.

Hydrogen Sulphide.—If hydrogen sulphide is applied to a copper sulphate solution, the copper is precipitated as cupric sulphide, and an amount of acid regenerated equal to that combined with the copper

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

If the solution is a chloride, a similar reaction takes place:

$$CuCl_2 + H_2S = CuS + 2HCl.$$

In either case, the regenerated acid solution is returned to the ore to dissolve more copper. The precipitated copper sulphide, like copper matte, may be brought to blister copper in converters. The escaping sulphur dioxide may be used in other stages of the process, either in the manufacture of sulphuric acid, or in the preparation of hydrogen sulphide.

Many wet methods of extracting copper from its ores have been based on the use of hydrogen sulphide as the precipitant. Most of these methods have as their fundamental idea, the inexpensive generation of the hydrogen sulphide, rather than a direct method of copper extraction.

At the Bede Metal Works the hydrogen sulphide was produced by treating sulphide of sodium with carbon dioxide, generated by burning coke in a shaft furnace. The sulphide of sodium was made from the acid mother liquor from which the sulphide of copper had been precipitated, by evaporating to dryness in a reverberatory furnace, mixing the residue with coal dust and reducing it in a similar furnace. This product, consisting of sulphide and carbonate of soda, was leached, and the solution treated with carbon dioxide. The carbonate of soda was produced as a by-product of the process.

Hydrogen sulphide, according to Schnabel,[1] is best generated by leading sulphur dioxide and water vapor over red hot coke or charcoal. For this purpose the gases produced in roasting sulphides in pyrite burners or kilns are aspirated by means of Korting injectors, and forced together with the steam from the injectors through a shaft furnace filled with glowing charcoal or coke. The sulphur dioxide is reduced to sulphur by the carbon; the water vapor forms with the red hot carbon, hydrogen and carbon monoxide, and the hydrogen and sulphur combine to form hydrogen sulphide. The coke or charcoal is kept hot by injecting a stream of air from time to time as in the production of water gas.

A method devised by Sinding depends upon the action of sulphur vapor on hydrocarbons and hydrogen; another on the decomposition of sodium sulphide by carbon dioxide. Sinding generates producer gas with raw fuel, and leads it over red hot pyrites; by the action of the hydrocarbons and the hydrogen contained in producer gas upon the sulphur evolved from the pyrites, hydrogen sulphide is formed, and is made to

[1] Handbook of Metallurgy, Vol. I, p. 209.

traverse a chamber in which the cupriferous solution is dropping down in the form of rain.

Gill and Gelstharp produced hydrogen sulphide by the action of carbon dioxide on sodium sulphide.

In the application of hydrogen sulphide to the precipitation of copper solutions, the precipitation is thorough and complete. If the solution contains gold and silver, the filtrate will never assay more than a trace; that is to say, less than 0.0005 oz. or 1 cent per ton. The conditions for thorough precipitation in a normally working plant, are that the solution should be slightly acid, or if neutral, contain an excess of free chlorine or ferric salts. If the solution is alkaline or neutral, the precipitation of the copper, gold and silver will be complete, but some of the undesirable elements will be thrown down with them. The precipitate is voluminous and may be difficult to filter. If the solution is neutral and contains a large excess of chlorine or ferric salts, the hydrogen sulphide reacting with these substances, will reduce them, and acidify the solution sufficiently to prevent the baser metals from being precipitated.

$$Cl + H_2S = 2HCl + S,$$
$$2FeCl_3 + H_2S = 2HCl + 2FeCl_2 + S,$$
$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S,$$

and thus hydrogen sulphide will be consumed, an equivalent of acid regenerated, and elemental sulphur precipitated with the copper sulphide.

The metals of the alkalies and alkaline earths are not precipitated from either the acid or alkaline solutions. Frequently compounds of calcium and aluminum will be found in the precipitate. Calcium sulphate is only slightly soluble in water, but is somewhat soluble in chloride solutions, and unless the solution is thoroughly settled or filtered, it is also likely to be carried into the precipitate by suspension. If the ore contains much alumina and the solution issuing from the leaching tanks is neutral or alkaline, a white gelatinous substance, probably aluminum hydroxide, settles out of the clear or milky solution, and may in this way get into the precipitate. On the addition of acid this precipitate is redissolved and the solution becomes clear.

Metals which are precipitated by hydrogen sulphide, as sulphide, from a solution of their salts in the presence of free acid, are:

Platinum,	color of precipitate,	dark brown.
Gold,	color of precipitate,	dark brown.
Silver,	color of precipitate,	black.
Copper,	color of precipitate,	black.
Lead,	color of precipitate,	black.
Tin,	color of precipitate,	yellow-brown.
Antimony,	color of precipitate,	orange.
Arsenic,	color of precipitate,	yellow.
Mercury,	color of precipitate,	black.
Cadmium,	color of precipitate,	yellow.

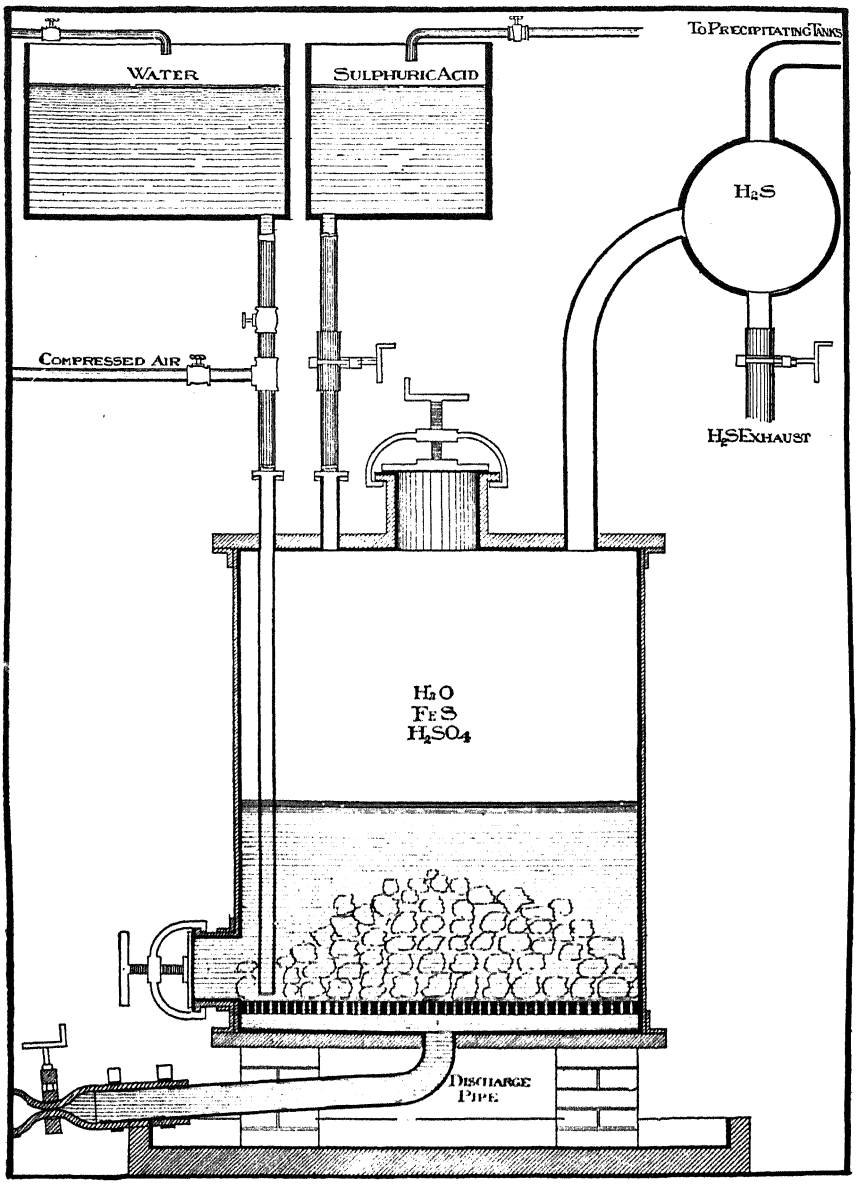


Fig. 53.—Hydrogen sulphide generator.

The hydrogen sulphide employed in precipitation is usually generated from iron sulphide (FeS), sulphuric acid, and water. A solution having a large excess of acid will require more hydrogen sulphide to precipitate the metals than one only slightly acid. A strongly acid solution will give a cleaner precipitate than a neutral solution, and give less trouble in the filter presses.

The hydrogen sulphide generator, for producing the gas on a large scale, from acid and matte, is shown in Fig. 53 and may be made of any size desired. It consists of an iron cylinder with flat cast-iron bottoms and tops. If the cylinder is small, it is made of cast iron; if large, of sheet steel. It is lined with lead, and all connections are made of lead pipe with burned joints. An equalizing tank, also made of lead, is located close to the generator.

The materials for generating the hydrogen sulphide are charged in the following proportions:

Iron sulphide (iron matte),	1 lb.
Sulphuric acid,	2.5 lb.
Water (approximately),	6 lb.

The total quantity of chemicals charged, will depend on the size of the generator, and the amount of metal to be precipitated.

In charging the generator, the exhaust valve from the equalizing tank is left open. The required amount of water is then introduced. This may be measured in a small tank over the generator, or it may be run in through the water pipe, or hose inserted into the manhole, to a certain depth which has been determined before hand as the right quantity of water for any required charge. The iron sulphide, broken into pieces about the size of hens' eggs, is dropped in through the manhole, which is then closed. The required amount of acid, which had previously been measured into the small lead tank located over the generator, is then run in and the valve again immediately closed. The generation of hydrogen sulphide begins at once. The exhaust valve on the equalizing tank, which was left open so that the pressure generated by the gas would not prevent the acid from flowing into the generator, is then closed. The increasing pressure will soon force the gas into the copper precipitating tanks.

Iron sulphide reacts with sulphuric acid to form hydrogen sulphide:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The gas so obtained always contains free hydrogen, owing to the presence of uncombined iron in the iron sulphide.

Compressed air is used to force the gas from the generator into the precipitating tanks and agitate the solutions.

After the precipitated solution has settled long enough to clarify, usually from 4 to 8 hours, it is decanted through the collar in the bottom

of the settling tank, into a filter press, and the clear regenerated solution may then be returned to the ore to dissolve more copper.

Lime.—Lime, calcium hydrate or milk of lime, is not suitable for precipitation from sulphate solutions. It has been used in precipitating copper from cupric and cuprous chloride solutions, calcium chloride being produced.

Milk of lime precipitates cupric hydrate from cupric chloride, and cuprous oxide from cuprous chloride. It throws down copper as cupric hydrate from a solution of the sulphate, but the precipitate is mixed with the insoluble calcium sulphate, which is formed at the same time, and gives a mixture which is very voluminous and very troublesome to smelt. The precipitation of the copper with lime from cuprous chloride was for a long time used in connection with the Hunt and Douglas process, in which the resulting calcium chloride was used in another step in the process, but lime has nowhere been regularly used to precipitate copper from sulphate solutions.

CHAPTER XII

ELECTROLYTIC PROCESSES

General Consideration of Electrolytic Methods.

Definitions.—*Electrolysis* may be defined as the decomposition of a chemical compound by the electric current. The compound may be in aqueous or igneous solution.

Electrolyte is a chemical compound in aqueous or igneous solution being decomposed by the electric current.

Electrode is a conductor to convey the current of electricity into or out of the electrolyte.

Anode is the electrode by means of which the current enters the electrolyte.

Cathode is the electrode by means of which the current leaves the electrolyte.

Ions are the constituent elements or radicals which carry the current of electricity through the electrolyte.

Anions are the elements or radicals which appear at the anode.

Cathions are the elements or radicals which appear at the cathode.

Electrolyzer is the apparatus by means of which or in which the electrolysis takes place.

Diaphragm is a partition, permeable or impermeable, between the anode and cathode, which permits the passage of the electric current but prevents the mixing of the electrolytes in which the anodes and cathodes are immersed.

Anolyte is the electrolyte in the anode compartment of the electrolyzer.

Catholyte is the electrolyte in the cathode compartment of the electrolyzer.

Current Density is the quantity of current, *i.e.*, the number of amperes, flowing through a unit of electrode surface.

Current Efficiency is determined by the yield per ampere.

Energy Efficiency is determined by the decomposition per watt.

Watt.—A watt is the product of one ampere multiplied by one volt.

Horse-power is the equivalent of 746 watts, and is approximately equal to 3/4 kilowatt.

Kilowatt is 1000 watts, and is approximately equal to 1 1/3 h. p.

Columb.—One ampere of electricity flowing for one second.

Electrolysis has been made the basis of a number of processes of extracting copper from its ores. Ever since success was achieved in electrolytic refining of blister copper, metallurgists have naturally asked why similar operations could not be successfully applied in the extraction of copper direct from its ores. At first thought the matter seems simple enough, but there are difficulties in the way of extracting copper from its ores which are not encountered in electrolytic refining. These difficulties, however, do not appear to be insurmountable, and it is quite probable that electrolytic methods of extraction will be in general use in the near future. Many of the difficulties, first met with, have been surmounted, and the remaining ones are gradually being overcome.

Anode.—One of the fundamental differences between electrolytic refining and electrolytic extraction, lies in the anode. In electrolytic refining the anode is a slab of blister copper, usually about an inch thick, and containing less than 1 per cent. of foreign matter. This copper anode goes into solution and is redeposited on the cathode. Theoretically, no energy is required to perform this work, since the energy developed in dissolving the copper anode is equivalent to that consumed in its deposition on the cathode. The soluble anode presents no serious difficulty. It has to be replaced at frequent intervals. Theoretically, no acid is consumed and none generated in electrolytic refining, since the acid going into combination with the copper at the anode is again released as free acid by its deposition at the cathode.

When copper is dissolved from the ore, conditions are entirely different. The problem then is, to deposit the copper out of solution by electrolysis while none is going into solution. This manifestly involves the use of an anode which will conduct the electricity into the copper solution, while at the same time the anode itself remains unattacked, or insoluble. This presents the first serious difficulty in precipitating copper from leaching solutions.

It has been found a most difficult matter to provide a substance which will be a good conductor of electricity and not be attacked by the combined action of the current and the solvent. Many substances which are sufficiently permanent, have too high a resistance, and consequently the power required to overcome this resistance in the anode, makes the process so expensive as to be prohibitive; while on the other hand, substances which have a good electrical conductivity are not sufficiently permanent. For chloride solutions this problem of suitable anodes has been satisfactorily solved by the use of graphitized carbon, but for sulphate solutions no really satisfactory anode has yet been discovered, although most conceivable substances have been tried. Lead, on the whole, has given the best results for sulphate solutions. The purity of the lead is an important factor.

Platinum is too costly for any process operated on a working basis.

All other commercial metals are attacked, and even platinum is not entirely unaffected. Ferro-silicon, which is a difficultly attackable substance, has been repeatedly suggested, but has not proved successful in practice. Antimonial lead has been tried for sulphate solutions, but there is no evidence to indicate that it is more permanent than pure lead; the antimony from the lead, going into solution in the electrolyte, may be objectionable and its loss by the decomposition of the anode, may be a serious item of expense. In almost all cases carbon is the only substance which can be employed in chloride solutions, but for sulphate solutions it is absolutely worthless.

The quality of carbons for electrolytic work varies considerably, but even the best are eventually destroyed. Graphitized carbons have given satisfactory results with chloride, but not with sulphate, solutions. These carbons, in addition to being durable, are good conductors of electricity. They possess a specific resistance of but 0.00032 ohm per cubic inch, which is only one-fourth that of amorphous carbon. The specific resistance is 0.000813 ohm per cubic centimeter, and since that of mercury is 0.000094 ohm, the conductivity is 11.75, mercury being 100; or 0.21, copper being 100. In some cases graphitized carbons have been used for 3 years as anodes in the decomposition of alkali metal chloride solutions, with a current density of 50 to 250 amperes per square meter. It is essential, however, that the solution be acid; in alkaline or neutral solutions, they are not as durable. The following is a list of standard sizes and weights of Acheson-Graphite electrodes:

ACHESON-GRAPHITE ELECTRODES

Size	Approximate weight per piece
Round:	
$\frac{1}{8}$ in. diam. × 12 in.,	0.008 lb.
$\frac{1}{4}$ in. diam. × 12 in.,	0.035 lb.
$\frac{3}{8}$ in. diam. × 24 in.,	0.15 lb.
$\frac{7}{16}$ in. diam. × 24 in.,	0.21 lb.
$\frac{1}{2}$ in. diam. × 24 in.,	0.26 lb.
$\frac{5}{8}$ in. diam. × 24 in.,	0.40 lb.
$\frac{3}{4}$ in. diam. × 24 in.,	0.60 lb.
$\frac{7}{8}$ in. diam. × 24 in.,	0.82 lb.
1 in. diam. × 24 in.,	1.00 lb.
$1\frac{1}{8}$ in. diam. × 24 in.,	1.40 lb.
$1\frac{1}{4}$ in. diam. × 24 in.,	1.75 lb.
$1\frac{1}{2}$ in. diam. × 24 in.,	2.60 lb.
2 in. diam. × 24 in.,	4.50 lb.
3 in. diam. × 40 in.,	16.60 lb.
4 in. diam. × 40 in.,	30.00 lb.
$5\frac{1}{8}$ in. diam. × $19\frac{1}{2}$ in.,	23.50 lb.
6 in. diam. × 48 in.,	75.00 lb.
8 in. diam. × 48 in.,	132.00 lb.

ACHESON-GRAPHITE ELECTRODES.—*Continued*

Size	Approximate weight per piece
Square:	
2×2×30 in.,	7.50 lb.
4×4×40 in.,	37.00 lb.
6×6×40 in.,	84.50 lb.
Rectangular:	
½×12×12 in.,	2.10 lb.
½×4 ×24 in.,	2.94 lb.
½×6 ×24 in.,	4.50 lb.
½×12×12 in.,	4.05 lb.
¾×3½×19½ in.,	3.13 lb.
¾×5 ×18 in.,	4.21 lb.
¾×12×12 in.,	6.75 lb.
⅞×2 ×21¼ in.,	2.20 lb.
1 ×4 ×30 in.,	7.50 lb.
1 ×6 ×30 in.,	11.30 lb.
1¼×3 ×36 in.,	7.88 lb.
1¼×5 ×30 in.,	11.50 lb.
2 ×4 ×30 in.,	14.50 lb.
2 ×7 ×30 in.,	25.75 lb.
3 ×6 ×30 in.,	33.25 lb.
4 ×8¾×15 in.,	31.45 lb.

These electrodes cost approximately from $13.50 to $15.00 per 100 lb. in lots of 500 lb. for the sizes most convenient for electrolytic use. In ton lots the cost would be approximately $11.50 per 100 lb.

Cathodes.—The cathodes used in electro deposition are usually thin sheets of pure copper. Carbon cathodes, in chloride solutions, do very well but are not advisable for sulphate solutions. If copper cathode sheets are used, they may be stripped after the deposit has acquired the desired thickness, or new sheets may be supplied as the old ones are removed. Lead cathode sheets have been used, and the copper stripped from the lead, or, the lead may be melted from the copper after removal from the electrolyzers, and again rolled into sheet lead for new cathode sheets.

In depositing copper from impure solutions, that is to say, solutions like those obtained in leaching copper ores, it is not an easy matter to get a reguline deposit of the desired thickness. Unless considerable care is taken with the electrolyte and the current density, irregular deposition and sprouting will occur long before the cathodes have acquired the thickness desired for their removal. This difficulty may be so aggravated as to make their removal necessary at an early stage of the operation, and thus adding considerable to the expense. If the cathodes, under such conditions, are not removed, the difficulty is quickly aggravated and short circuiting and inefficiency are likely to result. With a reasonably pure solution and low current density, this difficulty is not likely to occur,

especially if the solution is agitated or if the cathode is moved through the electrolyte. The current density, as well as the nature of the electrolyte, has much to do with the quality of the deposit; the lower the current density, the more reguline the deposit is likely to be, but there is a minimum practical limit to the current density that can be employed.

Diaphragms.—Most of the electrolytic processes are based on the fact that the solvent may be regenerated during electrolysis. If the solution electrolyzed at the cathode requires to be kept separated from that at the anode, then diaphragms are necessarily inserted between the anode and cathode, which, while allowing the free passage of the current, will prevent the solutions from mixing. Or if the electrolyte contains a large amount of an oxidizable and reducible metal under the anodic and cathodic influences, it may be desirable to use diaphragms, simply to overcome the undue loss in electrical efficiency. If copper sulphate solution, containing much iron sulphate is electrolyzed, considerable energy may be consumed in the oxidation and reduction of the iron, which simply renders an equivalent in useless heat.

Various materials may be used for diaphragms, but not many fulfill the conditions of low electrical resistance combined with sufficient density to prevent the anode and cathode solutions from mixing too freely. The material best suited for diaphragms is asbestos, which is not easily attacked either by acid or alkaline solutions, and when saturated with the electrolyte, offers no appreciable resistance at low current densities. At high current densities, any diaphragm is likely to offer appreciable resistance. Asbestos, suitable for diaphragms, is manufactured either as cloth, paper, or mill board. Asbestos cloth will give the best results if it is not necessary to make an absolute separation between the anolyte and catholyte. When complete separation is necessary it is desirable to use mill board or asbestos paper in connection with asbestos cloth. In whatever form the asbestos is used, it is desirable that it be quite free from foreign matter or admixtures.

While the construction of suitable diaphragms is not an insurmountable difficulty, it is desirable to dispense with them wherever practicable. The insertion of diaphragms in the electrolyzer also presents difficulties, as well as the construction of the diaphragm itself. In a copper electrolyte the ordinary materials of construction cannot be used, and hence to employ materials to take the place of the ordinary iron nails and bolts is more or less expensive. Ordinary porous clay, such as is used in battery jars makes a good diaphram to keep the solutions separate, but its electrical resistance is too high to be used in practice, and it must be used in sizes too small for economic adaptation.

It is evident that a diaphragm if it is to fulfill its purpose, its solid particles must not carry any current, since otherwise the diaphragm would not act as a diaphragm, but as a bipolar electrode. The current

passes through the interstices of the solid particles which compose the diaphragm, and the resistance of the diaphragm is the composite resistance of all the innumerable passageways of the electrolyte through the pores of the diaphragm. Diaphragms should be easily permeable to charged ions but should offer a high resistance to diffusion.

In Denver, at the Greenawalt experimental plant, were used some years ago, on a large scale, diaphragms made of asbestos cloth, asbestos paper, or mill board, or a combination of these, sandwiched between perforated boards from 1/2 to 3/4 in. thick. The perforations were about 1/2 in. in diameter and as close as possible, consistent with strength. The boards, with the asbestos between, were fastened together with wooden dowel pins and keyed. These diaphragms were expensive, and as the perforations did not exceed half the total area, only about half the diaphragm was effective. Diaphragms constructed in this way, must of necessity be small. Their use was discontinued.

Later, W. E. Greenawalt constructed diaphrams which were used in copper electro deposition, and were built 13 ft. 6 in. long by 3 ft. wide, made of two sheets of asbestos cloth, between which were sandwiched the desired thickness of asbestos paper, and these in turn, were sandwiched between two mullioned oak frames, bolted together with copper bolts. These diaphragms gave satisfactory results, but were later discarded when it was found that for the process under demonstration, diaphrangs could be dispensed with entirely.

Betts states that the best diaphragm he knows of for ordinary weak acid solutions may be made as follows:[1] Powdered sulphur is sifted evenly over a 1/4-in. asbestos mill board and the sheet heated evenly an hour or so just above the melting point of sulphur. The operation is then repeated with the other side. It takes from 1/4 to 3/4 lb. of sulphur to the square foot of mill board. This diaphragm is plastic when heated and in solutions does not soften at all. It expands slightly, and should be kept in acid water two or three weeks before using in any kind of rigid construction. The resistance is somewhat higher than without the sulphur, but the diffusion is smaller.

Current Density.—The current density has much to do with the efficiency of the operation and the nature of the copper deposited. It is not possible, in electrolyzing impure leaching solutions, to use as high a current density as in electrolytic refining, owing principally to the impurities, and to some extent the leaner copper content. If a reguline deposit is desired, it will be necessary to use a rather low current density. In electrolytic decomposition high current density causes impoverishment of ions at the electrodes and causes trouble. This impoverishment is prevented by stirring the electrolyte or moving the electrodes.

The energy efficiency becomes less as the current density is increased,

[1] "Electrochemical Industry," July, 1908.

and the theoretical voltage is only approached at very low current densities. If the voltage for a certain electrolyte, for example, is 1.2 at 5 amperes per square foot, at a current density of 30 amperes per square foot it is very likely to be three times that. Or, in other words, the energy efficiency at a current density of 30 amperes per square foot, is likely to be only one-third that at 5 amperes per square foot, assuming, of course, that the amount of copper deposited is the same in both cases, which may be a gratuitous assumption. It follows, further, that while the electrolytic deposition of the copper will take three times the power at 30 amperes per square foot as it would for 5 amperes per square foot, the size of the plant would be only one-sixth as large, and presumably cost only one-sixth as much.

The lower current densities will be largely limited to the cost and size of installation for the same output, and the larger current densities by the cost of operation.

The cost of power will be a governing factor in deciding the current density to be employed. If power is cheap it will probably cost no more to operate at a fair current density than at a low current density; for while the power, per pound of copper, will cost more, this will be offset by the decreased cost of installation, maintenance, and attendance.

If high current densities are employed, it will be desirable to agitate the electrolyte, or employ some form of moving cathode, so as to bring sufficient copper ions in contact with the cathode and thus avoid useless expenditure of energy in the decomposition of other substances in the electrolyte, or even the electrolyte itself.

It was observed soon after practical attempts were made at copper refining, about the year 1865, that the current density, and consequently the rate of deposition could be considerably increased by circulating the electrolyte or moving the electrodes.

Wilde was one of the first to deposit copper on a revolving cathode. The anodes consisted of copper cylindrical tubes, and the cathode consisted of an iron cylinder which was to be coated with copper. The cathode was placed in the center of the electrolyzer and rotated on its axis. This gave an even distribution of the copper over the entire cathode surface by means of the motion imparted to the solution and the equal current density resulting from the motion. The current density used was about 20 amperes per square foot.

Elmore used horizontal mandrels on which copper sheets or tubes are deposited, while agate burnishers travel continuously over the copper so as to consolidate it and at the same time prevent the growth of copper trees or nodules. The current density used was about 30 amperes per square foot.

Dumoulin introduced a process for burnishing copper, during deposition, with sheepskin as a substitute for agate. He claimed that the

process had the additional advantage of insulating any projections that might be formed on the deposited metal. It was claimed that a current of from 30 to 40 amperes per square foot of cathode surface could be used with a difference of potential of 1.6 volts, using a soluble copper anode.

Cowper-Coles gets excellent deposits of any desired thickness by revolving a cylinder cathode at a speed of from 1500 to 2000 lin. ft. per minute, with a current density of 200 amperes per square foot.

Attempts have been made at various times to increase the rate of copper deposition by Swan, Elmore, Thofern, Graham, Poore, and others by impinging jets of the electrolyte against a cathode surface. The quality of the deposits is likely to be unsatisfactory if impinging jets are alone employed; it is desirable, therefore, to move the cathode also, in order that the deposited copper may be uniform over its entire surface.

Whatever the means employed to increase the rate of deposition, the essential object to be attained is to bring sufficient copper ions in contact with the cathode, corresponding to the increased current, and to get a reguline deposit by friction either with the electrolyte or burnisher.

General Laws Governing the Electrodeposition of Copper.—In the decomposition of copper solutions, work is performed and energy consumed. The factors governing the expenditure of energy, in electrolysis, are

The electromotive force,
The resistance, and,
The current.

The electromotive force (e. m. f.) is measured in volts; the resistance in ohms, and the current in amperes. A definite relation exists between these three factors, whereby the value of any factor may always be calculated when the value of the other two are known. This relation is known as Ohm's law, and may be stated thus:

The current strength in any circuit is equal to the electromotive force applied to the circuit, divided by the resistance of the current. Or more briefly stated:

$$\text{Current} = \frac{\text{Pressure}}{\text{Resistance}} \text{ or}$$

$$\text{Amperes} = \frac{\text{Volts}}{\text{Ohms}} \text{ or}$$

$$C = \frac{E}{R}$$

In other words, the electromotive force (e. m. f.) which may be assumed to be the electrical pressure by the dynamo, causes the flow of an electric current. The current is directly proportional to the electromotive force. The resistance (electrical conductors and electrolyte) oppose

the flow of the current. The current is therefore proportional to the electromotive force.

The current strength in any circuit increases or decreases directly as the electromotive force increases or decreases, when the current is constant. With a constant pressure the current increases as the resistance is decreased, and decreases as the resistance is increased; or briefly, the current varies directly as the electromotive force and inversely as the resistance.

From this it follows, that to double the resistance halves the current, the electromotive force remaining constant. Or, if with the doubled resistance the current is to remain constant, the electromotive force, and consequently the power, must be doubled.

It also follows from Ohm's law that when through a given resistance the current is required to be doubled, the power must be increased four times; or in general, the resistance remaining constant the power increases proportionately to the square of the current.

Ohm's law, applied to the deposition of copper, means that, theoretically, the least power is required to deposit a given amount of copper when the lowest possible current density is used. This would require in practice, a plant of unlimited size, so that a well designed plant must of necessity be a compromise between theoretical conditions and practical requirements.

The Electrical Power is the product of the number of volts multiplied by the number of amperes of the current. Its unit is the *Watt*. 746 watts make a horse power; 1000 watts a kilowatt. Either the horse power or the kilowatt may be taken as the unit of power; the kilowatt is the most convenient in electrical and electrolytic work.

The power consumed in depositing a definite amount of copper may be expressed in horse power, thus:

$$\text{h. p.} = \frac{\text{Volts} \times \text{Amperes}}{746}.$$

and in kilowatts,

$$\text{k. w.} = \frac{\text{Volts} \times \text{Amperes}}{1000}.$$

The most important laws in relation to electrolysis are those of Faraday. His law of electrolysis may be stated thus:

Faraday's Law.—1. *The amount of chemical change produced electrolytically by the current is proportional only to the amount of electricity passing, as measured in columbs, and is independent of the strength or temperature of the electrolyte, or the size or distance apart of the electrodes.*

2. *The amount of different elements dissolved or set free by the passage of a given amount of electricity is proportional to their chemical equivalents.* Or in other words, the amount of electrochemical action produced is

directly proportional to the product of ampere hours and the chemical equivalents.

A given quantity of current, therefore, will always deposit the same quantity of a given element, and the elements are deposited proportionally to their chemical equivalents; as for example, hydrogen 1, oxygen 8, chlorine 35.5, cupric copper 31.75, cuprous copper 63.5, etc.

The "Chemical Equivalent" is the quotient $\frac{\text{Atomic weight}}{\text{valency}}$. The electrochemical equivalent of a substance is identical in weight with the amount of the same substance that would be deposited by 1 ampere in 1 second (that is, 1 columb). The electrochemical equivalent of any element may be calculated by multiplying the chemical equivalent of the element by .000010384, which is the electrochemical equivalent of hydrogen. For cupric copper it is 0.0003297 and for cuprous copper it is 0.0006594 (grams per columb).

Theoretical Data for Copper Deposition.—Theoretically 1.1858 grm. of copper are deposited by 1 ampere-hour from cupric, and 2.3717 grm. per ampere-hour from cuprous solutions. This for practical purposes would mean that 1 ampere should deposit 1 oz. of copper from cupric solutions, and 2 oz. from cuprous solutions, per day of 24 hours. From this it is easy to compare the current efficiency of any process or operation with the theoretical amount, which may be taken as 100 per cent.

The following theoretical depositions of copper, referred to various units, will be found convenient for reference:

One ampere-hour will deposit, theoretically, 1.1858 grm. of copper from cupric solutions, and 2.3717 grm. from cuprous solutions.

0.8433 ampere-hours will deposit 1 grm. of copper from cupric solutions, while 0.42164 ampere-hours will deposit 1 grm. from cuprous solutions.

One ampere-hour will deposit 0.02614 lb. of copper from cupric solutions and 0.05228 lb. from cuprous solutions.

382.50 ampere-hours will deposit 1 lb. of copper from cupric solutions; 191.25 ampere-hours will deposit a pound of copper from cuprous solutions.

746 ampere-hours will deposit 1.9494.lb. of copper from cupric, and 3.8988 lb. from cuprous solutions.

1000 ampere-hours will deposit 2.6143 lb. of copper from cupric, and 5.229 from cuprous solutions.

These statements of deposition do not take into consideration the voltage at which the current is delivered. It simply represents the amount of copper irrespective of the voltage. While the current efficiency of a process may be determined from the above theoretical quantities, the energy efficiency can only be determined when the theoretical as well as the practical voltage is known.

The theoretical voltage is proportional to the heats of combination of the compounds decomposed, and may be calculated from the molecular heats of combination as a basis. For cupric sulphate it is 1.22 volts; for cupric chloride it is 1.35 volts, and for cuprous chloride it is 1.42 volts. Blount[1] found by actual experiment in his laboratory that the minimum pressure necessary for the deposition of copper from cupric sulphate, using an insoluble anode, is 1.375 volts.

Knowing the theoretical deposition of copper by a definite amount of electric current, and the theoretical voltage as determined from the heats of combination, the theoretical power consumed in electrodeposition may readily be calculated, and this is taken as the standard of the energy efficiency, or 100 per cent., to which all practical energy efficiencies may be referred, since that represents the greatest possible amount of copper that can be deposited with a given amount of electrical energy. It represents the greatest amount of copper that can be deposited with a definite current, and the lowest possible voltage at which it can be deposited.

The following tabulated statement, gives in convenient form, the theoretical energy required to deposit copper, with insoluble anodes, from cupric sulphate, cupric chloride, and cuprous chloride solutions, based on the molecular heats of combination.

Electrolyte	Grm. per h. p.-hour	Grm. per k. w.-hour	Lb. per h. p.-hour	Lb. per k. w.-hour	Lb. per h. p. day	Lb. per h. p. day
Cupric sulphate....	726	972	1.5979	2.1429	38.35	51.43
Cupric chloride....	656	878	1.4440	1.9440	34.66	46.66
Cuprous chloride....	1246	1670	2.7451	3.6824	65.88	88.38

To determine the actual current and energy efficiencies of copper deposition in an electrolytic process, the current is accurately measured both as to quantity and pressure—amperes and volts—for a certain definite time. The amperes multiplied by the volts, gives the watts; 746 watts is equal to a horse-power, and 1000 watts to a kilowatt. The copper deposited is carefully collected, dried, weighed and assayed to determine its purity. The weight of the pure copper deposited by the current and the power consumed, compared with the theoretical, gives the current and energy efficiencies.

For Example.—In making a certain test on the electrodeposition of copper from a cuprous solution, a current of 400 amperes was used for 12 hours (4800 ampere-hours), at 1.8 volts. The pure copper recovered was 18.2 lb. The theoretical amount that should have been deposited at the rate of 5.229 lb. per 1000 ampere-hours, is 25.1 lb. The test, there-

[1] "Practical Electro-Chemistry," p. 64, 1906.

fore, showed a current efficiency of 72.5 per cent. The copper deposited in the test was at the rate of 2.15 lb. per k. w.-hour; the theoretical deposition per k. w.-hour is 3.6824 lb.; hence the energy efficiency is 58.2 per cent. As compared with the deposition from cupric solutions, however, this test would show a current efficiency of 145 per cent. and an energy efficiency of 116.4 per cent.

In practical electrolytic work it is rarely that 90 per cent. is exceeded for the current efficiency, and 50 per cent. for the energy efficiency. It will usually be found profitable to sacrifice electrical efficiency for other considerations.

In many processes, the secondary anode reactions tend to reduce the theoretical voltage; this may vitally effect the energy efficiencies as above given, because the secondary reactions must be taken into consideration in figuring the energy efficiency for any particular process, when such reactions are involved. In the Hoepfner process, for example, the theoretical voltage for the decomposition of cuprous chloride is 1.42 volts, but this is to some extent offset by the recombination of the released chlorine at the anode, combining with the cuprous chloride to form cupric chloride, so that the theoretical voltage is only 0.18 volt, instead of 1.42 volts, or only about one-eighth. The theoretical deposition, taking into account the secondary reaction, would be 697.2 lb. of copper per k. w.-day of 24 hours instead of 88.38 as given in the table. A similar reduction of voltage is theoretically possible in the Siemens-Halse process as also in processes using sulphur dioxide to combine with chlorine or sulphion at the anode. It must be evident, however, that these reductions of voltage due to secondary reactions, are more apparent than real, largely because an impracticable small current density must be employed for their realization, or even an approach at realization, although Hoepfner claimed a practical voltage of 0.8 volt in the operation of his process; but Hoepfner used an exceedingly low current density.

Loss of Energy in Electrolytic Work: Joule's Law.—Much of the energy consumed in electrolytic work, both in the conductors and electrolyte, appears as heat. Joule first discovered that the development of heat was proportional to:

1. The resistance of the conductor;
2. The square of the current;
3. The time during which the current flows.

When heat is thus produced in the conductors and the electrolyte it is a waste of power. The current density both in the electrolyte and in the conductors may seriously affect the heating of the circuit, and consequently the ultimate voltage at the dynamo. The conductors should, therefore, be amply large to carry the current, and the electrical connections should be as few as possible, and all connections should be well

made. At the Anaconda Copper Refinery it was found on careful investigation, that 20 per cent. of the loss of efficiency was in the conductor connections.

A considerable percentage of the power used in electrodeposition of the copper may be lost in the metallic conductors, and contacts, especially if the conductors are of insufficient cross section and the connections poor.

For electrolytic refineries, which are presumably under at least good average conditions, Addicks[1] gives a rough summary of the relative value of the resistances in practice, as follows:

Metallic resistance,	15 per cent.
Electrolyte, including transfer,	60 per cent.
Contacts,	20 per cent.
Counter e. m. f.,	5 per cent.

Contact resistances are met with at the joints in the main bars and at the connections between the bars and the electrodes. The joints in the main bars should be equal in conductivity to the bar itself. This standard can be easily attained if the bars are properly faced. Three hundred to four hundred amperes per square inch of bearing area will give no trouble.

The counter electromotive force in copper refining, due to the greater concentration of the electrolyte at the anode than at the cathode is quite small, usually about 0.02 volt. Contacts for copper deposition from insoluble anodes are more likely to be source of loss of energy than in electrolytic refining, due to the considerably higher voltage between the electrodes. In copper refining the difference of potential between the electrodes is from 0.2 to 0.4 volt, while in copper deposition with insoluble anodes, it will vary in practice between 1.5 and 3 volts, depending largely on the current density employed.

The Electrolyte.—The solvents usually employed for electrolytic processes have either sulphuric or hydrochloric acid as the basis. The solvent, to a large extent, determines the details of the process. In the electro deposition, the solvent should be regenerated, as well as the copper precipitated. In leaching copper ores, therefore, repeatedly with the same solution all the soluble impurities in the ore are likely to be found in the electrolyte, and this is true, but not to the same extent, if the solution is used only once and then wasted, instead of being used repeatedly in the same cycle. The cycle will ordinarily consist of:

Solution,
Precipitation,
Regeneration;

[1] *The Journal of the Franklin Institute*, Dec., 1905.

and it is not likely that any electrolytic process can achieve marked success on any other basis. The regeneration may be direct; that is to say, take place in the electrolyzer and under the action of the current; or, the anode products may be withdrawn from the electrolyzer and then in some way combined with the solution.

Whatever method is adopted, the solution, in a cyclic process, is likely to become charged with impurities and thus reduce the efficiency of the deposition. Two alternatives present themselves; either to purify the solution, or waste it at intervals. If the solution is wasted, a small portion of it may be withdrawn at every cycle, and a corresponding amount of fresh water added. This can be done quite readily if there is more solvent regenerated in the process than is consumed by the ore.

Various methods have been suggested for purifying a foul electrolyte; these differ somewhat as a sulphate or a chloride solution is used.

The injurious effect of an impure electrolyte is shown more particularly in the electrolysis. The undesirable metals in the solution may be deposited with the copper if the solution has become impoverished, or else useless energy may be expended in reduction and oxidation, or in deposition and immediate solution, under the influence of the current.

A comparative measure of the energy required to deposit the various metals, is obtained by taking the heat of combination of the metals with oxygen, to form salts. Those metals are first deposited which have the lowest heat of combination, other things being equal. The order of deposition may be approximately stated as follows: gold, silver, copper, antimony, bismuth, arsenic, lead, nickel, cobalt, cadmium, tin, iron, zinc, manganese. The alkali metal salts, either the chlorides or sulphates, are only decomposed with considerable difficulty, nevertheless, when high current densities are employed they may frequently be the cause of considerable loss of efficiency.

Gold and silver will be deposited with the copper, and the deposition may take place either chemically or electrolytically. Neither gold nor silver are likely to be in sulphate solutions; both may be in chloride solutions.

The order of precipitation, as given, is dependent upon certain conditions which must be observed. Principally among these conditions are the strength of current, the nature of the electrolyte, the relative proportion of the metals in solution, and if the solution is low in copper, whether or not the electrolyte is agitated. If the current density, and consequently the voltage, exceeds a certain strength, all the metals, or several of them, may be deposited together. The more neutral the electrolyte is, the more easily will the more electropositive metals be deposited. The current is always striving to decompose the electrolyte into metal or oxide and acid or the acid radical; while the liberated acid is striving to redissolve the liberated metal or oxide. These two forces are

always opposed to one another, and under varying conditions either may gain the upper hand. The resolvent action of the acid, in cases where the components of the electrolyte have a strong chemical affinity, may overpower the action of a weak current.

In the deposition of copper this secondary reaction may not be of much importance in a sulphate electrolyte, but it is quite noticeable in the presence of good circulation of the electrolyte, and more or less access of air to the cathodes. With a chloride electrolyte this secondary reaction may be quite pronounced under certain conditions, especially if the electrolyte is violently agitated. With all of the easily dissolvable metals, it is this secondary reaction which prevents the metal from making its appearance at the cathode in metallic form, as the deposition, and solution due to secondary reaction, are practically simultaneous, and the operation simply results in a corresponding loss of efficiency.

It is evident that if the current density exceeds in amount that capable of being supplied with copper ions, other metals in the electrolyte are decomposed, and under aggravated conditions the electrolyte itself may be decomposed. The relative amounts of the various metals in solution also determines the efficiency of the process under certain conditions. If the electrolyte contains only a small amount of copper and considerable zinc—conditions quite likely to occur—the copper will be deposited to the exclusion of the zinc with a correspondingly low current density, but if that density is exceeded, the zinc will be electrolyzed, and if the electrolyte is quite acid it will be redissolved at the cathode as rapidly as deposited, with the net result that the copper will be permanently deposited at the cathode, but at a greatly increased expenditure of energy. If the metal at the cathode is not readily soluble in the electrolyte, the copper will be correspondingly impure.

When copper ores are leached with any acid solution, or a solution having an acid base, any or all of the metals may be in the solution, and when electrolyzed may be influenced by the current as described. As the electrolyte remains more acid, purer copper is likely to be deposited, but when it becomes neutral, or only slightly acid, the undesirable metals are deposited with the copper and are likely to remain on the cathode. Such a condition, however, is not likely to occur since a neutral, or only slightly acid solution, is not an energetic solvent of copper from its ores.

The principal factors which determine the kind of ion to be deposited on the cathode is the heat of formation of the different possible reactions; that reaction which absorbs the least energy occurs, in general, the most readily; but this statement is only approximately true. The concentration of the two electrolytes and the current density must be taken into consideration.

The heat of formation of the most important chlorides and sulphates

likely to be in the electrolyte from leaching copper ores, in dilute solutions, is as follows:

MOLECULAR HEATS OF FORMATION OF CHLORIDES AND SULPHATES IN DILUTE AQUEOUS SOLUTIONS

Chlorides		Sulphates	
NaCl,	96,600 calories	Na_2SO_4,	328,500
$CaCl_2$,	187,400 calories	$MgSO_4$,	321,100
$MgCl_2$,	187,100 calories	$CaSO_4$,	321,800
$MnCl_2$,	128,000 calories	$Al_2S_3O_{12}$,	879,700
$AlCl_3$,	238,100 calories	$MnSO_4$,	263,200
$ZnCl_2$,	113,000 calories	$ZnSO_4$,	248,000
$FeCl_2$,	100,100 calories	$FeSO_4$,	234,900
$FeCl_3$,	127,850 calories	$Fe_2S_3O_{12}$,	650,500
$PbCl_2$,	77,900 calories	$NiSO_4$,	228,700
CuCl,	35,400 calories	$PbSO_4$,	216,000
$CuCl_2$,	62,500 calories	$CuSO_4$,	197,500
$AsCl_3$,	71,500 calories	H_2SO_4,	210,200
$SbCl_3$,	91,400 calories	Ag_2SO_2,	162,600
$BiCl_3$,	90,800 calories		
AgCl,	29,000 calories		
$AuCl_3$,	27,200 calories	SO_3,	141,000
HCl,	39,400 calories	SO_2,	77,600
$NiCl_2$,	93,900 calories	H_2O,	69,000

The decomposition values are independent of the solution, in the case of bases and acids which on electrolytic decomposition evolve oxygen and hydrogen at the electrode, and this is true for all acids excepting those whose decomposition values are below the maximum. For these the value rises with increasing dilution, and finally reaches the maximum. This is very marked in the case of hydrochloric acid:

	Decomposition point
2n HCl,	1.26 volts
n HCl,	1.31 volts
1/2n HCl,	1.34 volts
1/6n HCl,	1.43 volts
1/16n HCl,	1.62 volts
1/32n HCl,	1.69 volts

With 1/32n HCl a point is reached where chlorine is no longer given off, but a large proportion of oxygen.

In leaching ores with sulphate solutions, the chlorides are not likely to present, but if a chloride solution is used, the sulphates are quite sure to be present, especially if the ore is roasted. The chlorides will be decomposed before the sulphates.

If, for instance, the electrolyte contains $CuCl_2$, $ZnCl_2$, and Na_2SO_4, either the Cu, Zn, or Na may be active in transporting the current through the solution, but the heat of combination of cupric chloride is 62,500 calories; that of zinc chloride 113,000 calories, and that of sodium

sulphate 328,500 calories, so that copper will be deposited to the exclusion of zinc until the minimum voltage for the electrolysis of zinc chloride is exceeded; then the zinc chloride may be decomposed if there are not enough copper ions in the solution to transport the current through the electrolyte, and finally even the sodium sulphate may be decomposed, if the voltage is sufficiently high. It is evident, however, even with impure electrolytes, copper may be deposited to the exclusion of other metals in appreciable amounts.

Effect of Bismuth, Arsenic, and Antimony, in the Electrolyte.—None of the metals highly injurious to copper, such as bismuth, arsenic and antimony, are likely to affect the deposited copper. These metals are largely eliminated in the cyclic operation of the process, even if contained originally in the ore. If the ore is a sulphide and has to be roasted, these elements are largely volatilized during the roasting. If they should accumulate in the solution, they are easily removed and their removal may be made to render an equivalent in acid by precipitating with hydrogen sulphide. Bismuth is not deposited on the cathode even when present in considerable quantities. Neither arsenic nor antimony are deposited with the copper unless the solution approaches neutrality.

Iron in the Electrolyte.—Iron is most likely to be in the electrolyte, as it always is associated with copper ores. In sulphate solutions the iron is likely to accumulate indefinitely, to saturation, unless the solution is purified at intervals. With chloride solutions, the iron chloride acts more or less on the copper compounds in the ore to form copper chloride, while the iron is precipitated as the insoluble ferric oxide. In the electrolysis of a copper sulphate solution, containing considerable iron sulphate, the iron passes from the ferrous to the ferric condition at the anode, and is transformed back again to the ferrous condition at the cathode, and thus using energy without rendering a useful equivalent. Similarly the ferrous chloride may be transformed to ferric chloride and back again, as the solution passes from anode to cathode, but in so doing the ferrous chloride is likely to be oxidized to the ferric oxide, under the oxidizing influence of the chlorine.

E. H. Larrison, aptly sums up the effect of iron sulphate in an electrolyte of copper sulphate as follows:[1]

"The process of electrolysis exercises in the main a reducing influence in an electrolyte of copper sulphate containing iron sulphate. Further reduction, and probably the retardation of the deposition of the copper, comes about through some such reaction as the following:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4.$$

That is, copper already deposited or on the point of being deposited is attacked by the ferric sulphate and dissolved thereby, also reducing the ferric to ferrous

[1] *E. and M. J.*, Sept. 7, 1907.

sulphate. When the process has gone on for some time the electrolyte becomes so dilute with respect to ferric sulphate that the last of the copper is able to keep its place upon the cathode. This accounts for the difficulty of, and the comparative great time necessary for the removal of the last few miligrams of copper from a solution high in iron. When using a stirrer and high current densities, a very small reduction in the current density is quickly followed by the re-solution of much of the deposited copper. It seems as if the copper is able to keep its place on the cathode only with a certain electrical or reducing tension.

"Circulation of the electrolyte not only allows the use of higher current densities, and thereby more rapid work, but it gives the current greater efficiency. This is not only due to the fact that the solution is kept uniform and the copper deposits more rapidly, but also the reducing effect of the iron is much greater and consequently the dissolving power of the solution is decreased much sooner. A very rapid method of reducing the iron before applying the current would save time.

"The influence of iron on copper electrolysis may be summed up as follows:

"1. High percentages of iron in the ferric condition materially retard copper deposition. Ferrous salts have little or no effect.

"2. The effect of the electric current in the usual solution is to reduce ferric salts to ferrous salts. This reduction must proceed to a certain point before all the copper will remain on the cathode. This point is about the same whatever the iron and copper percentages, but it varies some as the solution is circulated or stationary.

"3. Rapid circulation of the solution by a stirrer permits the use of high current densities without sponging, thereby making faster deposition. The current also is more efficient for both depositing copper and reducing iron."

Purification of the Electrolyte.—Various methods have been suggested for purifying the electrolyte, and these depend to a large extent on the nature of the solvent. Many are based on the practice of the electrolytic refineries.

The solution may be treated electrolytically by passing a current of electricity through it with a high current density at the cathodes, and employing either copper or lead anodes for sulphate solutions, and carbon anodes for chloride solutions. By this means many of the metallic impurities can be thrown down on the cathode, especially if the solution is not too highly acid.

At Anaconda a process was used which consisted in passing the impure electrolyte repeatedly through a layer of oxidized copper, so as to partially precipitate the antimony and bismuth. By this treatment the solution becomes nearly neutral, and saturated with copper, and was then oxidized by passing air through it, so that the iron is partially precipitated as ferric oxide.

Ulke states that one of the best methods for purifying old solutions is that in which it is electrolyzed in special vats, the anodes being of lead, and the cathodes of copper. A current density is employed sufficiently

great to deposit the arsenic and antimony, but not strong enough to deposit the iron. The solution thus freed from the arsenic and antimony is returned to the copper depositing vats to be used in the ordinary way, and this is repeated until the bath contains so much iron that it is necessary to remove it by crystallizing out the ferrous sulphate.

Ottaker Hofmann gives the following method of purifying copper sulphate solutions having in addition to the cupric sulphate, salts of iron, arsenic, antimony, bismuth, cobalt, nickel, etc.[1]

"The crude neutral cupric sulphate solution is forced into towers, about 6 ft. in diameter and 16 ft. high. These towers are lined with lead. A lead pipe, connecting with an air compressor, is led into the tower through the funnel-shaped bottom. Near the bottom is a lead steam coil for heating the solution.

"When the tower is filled with impure solution, obtained by treating roasted copper matte with dilute sulphuric acid, steam is allowed to enter the coil and heat the solution and at the same time air is forced through the pipe at the bottom. The ascending air imparts a violent boiling motion to the liquor. Part of the iron is precipitated as basic salt, by the action of the air. More than half the iron was never precipitated although the treatment was extended many hours. When the solution is hot (75 to 80° C.) roasted matte is added. The violent boiling motion of the solution keeps the matter in suspension, and after 3 or 4 hours the solution will be entirely free from iron, arsenic, antimony, bismuth, etc. To observe and regulate the progress of the operation the solution is tested from time to time for iron by taking samples through a small cock inserted in the sides of the tower. It is not necessary to test the solution for other impurities, because the iron predominates, and by the time all of it has been precipitated, no trace of the other impurities will be found."

"The chemical reaction of this process may be expressed as follows:

$$2FeSO_4 + O + CuO = Fe_2O_3 + 2CuSO_4.$$

This shows that the cupric oxide, which together with air, is used to precipitate the iron, combines with the sulphuric acid of the ferrous sulphate, and goes in solution as cupric sulphate; a decided advantage, as the precipitant is converted into cupric sulphate, and thus enriches the copper solution."

At the Kalakent Copper Works, Russia,[2] when the impurities in the electrolyte had accumulated to such an extent as to endanger the quality of the electrolytic copper, the foul solutions were withdrawn from the individual or group of tanks and regenerated, this regeneration being accomplished with considerable difficulty at first, but finally it was done advantageously as follows:

"The foul solutions were heated and passed over dead roasted matte fines, heaped in loose-bottomed trays arranged in series in upright rows. By this method all the sulphuric acid in solution, down to about 2 grm. per 100 c.c., was neutralized and combined with copper and iron. The solution was then allowed

[1] Mineral Industry, Vol. VIII, p. 192.

[2] Titus Ulke, "Modern Electrolytic Copper Refining," p. 145.

to trickle through heaps of roasted low-grade copper ores, which resulted in the almost complete neutralization of its acid contents. It was then diluted with washwaters down to 10 to 12° B. and heated, to free the solution from iron, arsenic, tin, and bismuth, in lead pans, which were provided with an appliance for injecting compressed air into the solution. Anode scrap was suspended in the pans so as to neutralize any remaining portion of acid, and to take up any new acid set free through the separation of iron hydrates, and thereby form copper sulphate. By blowing compressed air into the solution heated to about 50° C., the copper in the anode residue or scrap was quickly dissolved, and the separation of the iron, arsenic, antimony, tin, and bismuth, which occurred when the solution had been nearly or completely neutralized, accomplished. The solution was then concentrated up to 14 to 15° B. and clarified in special reservoirs. It now contained 3.5 to 4 grm. of copper per 100 c.c., and of impurities only 0.5 to 1 grm. iron, besides traces of zinc, nickel, and cobalt, and was therefore pure enough for reuse as electrolyte. The excess of purified electrolyte which gradually accumulated with this method of regeneration was eventually withdrawn from the circulating system and worked up into blue stone. The electrolytic copper possessed a purity of at least 99.9 per cent. by analysis, and averaged 99.93 per cent. copper."

If cupric sulphate is crystallized out of impure solutions and redissolved in water, it may be electrolyzed to deposit the copper and liberate the combined sulphuric acid. The acid solution may then be again applied to the ore, with all or most all of the impurities eliminated.

Hoepfner[1] proposed precipitating the impurities from a chloride solution with oxychloride of copper. In doing this, some of the cuprous chloride in the solution is converted into the oxychloride of copper by blowing air or oxygen into the electrolyte:

$$Cu_2Cl_2 + O = Cu_2Cl_2O.$$

"This is most conveniently done by cooling the solution, or a part thereof to precipitate the cuprous chloride, which is then converted into the oxychloride by contact with air. This solid precipitate is a most efficient reagent for iron and to enrich solutions poor in copper so as to make it more suitable for electrolysis. The reaction may be expressed as:

$$3Cu_2Cl_2O + 2FeCl_3 = 4CuCl_2 + Cu_2Cl_2 + Fe_2O_3.$$

Lime, the caustic alkalis or alkaline earths, or their carbonates, may be used as precipitants; or the oxides or carbonates of metals, as, for instance, of copper, may be employed in the separation of the undesirable metals from the electrolyte, the metals being precipitated according to the precipitant used in the form of oxide or in the form of arsenate and antimonate of iron or copper, the arsenic and antimony being present in the solution in the form of arsenious and antimonious acids, or arsenic and antimonic acids which are converted by the precipitant into insoluble arsenic and antimonic salts, while if an oxide or carbonate of copper is used the arsenic and antimony are converted into insoluble arsenate or

[1] U. S. Patents No. 507,130, Oct. 24, 1893, and No. 704,639, July 15, 1902.

arsenite of copper and the corresponding salts of antimony. Inasmuch as the electrolyte contains copper it may readily happen that the salts last referred to will be formed without the use of a copper salt when lime or an alkali is used as the precipitant. In either case, but a comparatively small proportion of the copper goes over with the precipitant, which quantity is in no case greater than the quantity of the arsenic and antimonic salts precipitated."

Greenawalt purposes purifying chloride solutions by electrolyzing common salt to form caustic soda and chlorine; the caustic soda is used as a precipitant of the impurities, and the chlorine to produce acid.

In purifying the electrolyte, a certain portion is withdrawn from the cycle of operation, and the caustic soda applied to it;

$$RCl_2 + 2NaOH = 2NaCl + R(OH)_2$$

in which R may represent any or all the base metals.

In this way the base metals are precipitated and the sodium chloride regenerated. The chlorine liberated by electrolysis of the salt is combined with sulphur dioxide, in the presence of water, or the solution, to form acid;

$$2Cl + SO_2 + 2H_2O = 2HCl + H_2SO_4.$$

In this way all the undesirable impurities are eliminated from the solution, and a corresponding amount of acid solution regenerated.

In the purification of the electrolyte it is generally assumed that a pure deposit of copper is necessary. If the impurities in the electrolyte do not materially interfere with the efficiency of the process it would be better to work with impure solutions even though an impure copper is deposited. There is no reason why the purity of the deposited copper should be a matter for serious consideration.

The relative efficiency of the process, due to impurities in the electrolyte is more serious than the relative purity of the copper. Some elements cause serious loss of efficiency if present in certain combinations, while in other combinations the loss cannot be considered of much consequence. Ferric salts, for example in the electrolyte, may cause a serious loss of efficiency, while ferrous salts are comparatively harmless. And this applies generally to the elements which have different valencies for different combinations, and which are capable of oxidation and reduction in the electrolyte due to electrolysis.

Depolarizers.—Various depolarizers have been suggested in connection with the electrodeposition of copper; among the most important is sulphur dioxide. The use of reducing gases, and particularly sulphur dioxide, for the depolarization of insoluble anodes in the deposition of copper, was described as long ago as 1878 by Cobly. Later Luckow used sulphur dioxide in the electrolysis of zinc solutions, and its application in more recent years has been quite common and well understood.

If cupric sulphate is electrolyzed:

$$CuSO_4 + \text{electric current} = Cu + SO_4.$$

The resulting products are copper at the cathode and sulphion at the anode. The liberation of the SO_4 at the anode immediately results in a secondary reaction,

$$SO_4 + H_2O = H_2SO_4 + O$$

whereby water combines with the sulphion to form sulphuric acid, while oxygen is released. If, however, sulphur dioxide is in the anode solution, the SO_4 and SO_2 combine, with water, to form two atoms of sulphuric acid,

$$SO_4 + SO_2 + 2H_2O = 2H_2SO_4$$

and, theoretically, no oxygen is released. This reaction develops a certain electromotive force at the anode, in the same direction as the current, and thus reduces the necessary voltage in the decomposition of the copper.

If sulphur dioxide is used in connection with chloride solutions, the electric current decomposes the copper chloride into copper and chlorine,

$$2CuCl + \text{electric current} = 2Cu + 2Cl.$$

The chlorine combining with the water,

$$2Cl + H_2O = 2HCl + O + 10{,}800 \text{ calories},$$

to produce hydrochloric acid and release oxygen, and thus chlorine may become an oxidizing agent. This reaction takes place very slowly, but the oxygen can immediately exert a further chemical action in the presence of sulphur dioxide, when a rapid decomposition of water takes place,

$$2Cl + SO_2 + 2H_2O = H_2SO_4 + 2HCl + 74{,}400 \text{ calories}$$

in which case the chlorine released at the anode is by secondary reaction, converted into sulphuric and hydrochloric acids with the development of 74,400 calories; which tends to reduce the voltage in the operation. Ordinarily, chlorine will be given off at the anode in the absence of sulphur dioxide, because the oxidizing action of chlorine is exceedingly slow; in the presence of sulphur dioxide the amount of chlorine released will depend upon the current density. If the current density is sufficiently low to permit of the released chlorine coming in contact with the sulphur dioxide before either can escape, no chlorine will appear, as such.

Other reactions have been suggested in the decomposition of copper compounds, acting on the principle of depolarizers. In Body's process, ferrous chloride is converted into ferric chloride by the chlorine released.

at the anode; in the Siemens-Halske process ferrous sulphate is reconverted to the ferric sulphate in the deposition of the copper from a solution of cupric and ferrous sulphates; and in the Hoepfner process, in which the copper is deposited from a cuprous chloride solution and a certain amount of the cuprous chloride converted back to the cupric chloride by the chlorine released at the anode.

In all of these reactions, the electromotive force developed works in the direction of the current and thus reduces the necessary voltage. The approximation of the theoretical to that realized in practice, depends on the conditions of operation, principally among these conditions is the current density. If the current density is so low as to permit all of the anode gases to combine with the depolarizer, the theoretical efficiency may be quite closely realized.

Rapid Deposition of Copper.—To rapidly deposit a metal from solution by the electric current, it is necessary that the metal ions be present in sufficient number at the cathode. If a comparatively high cathode density is used, the danger is that the electrolyte in proximity to the cathode becomes poor in the ions deposited, and other processes start, especially the development of hydrogen. To counter this tendency, it is necessary to artificially bring fresh electrolyte to the cathode surface, as for instance, by stirring, or rotating the cathode.

In an ordinary electrolyzer, if the electrolyte is not agitated or cathode rotated, as soon as the current is switched on, copper is deposited on the cathode and a thin layer of electrolyte touching the cathode becomes in consequence impoverished in copper. Before more deposition can take place this thin layer of exhausted electrolyte has to be removed. If left to itself, removal and changing will take place quite slowly, nevertheless it will be fast enough to supply sufficient copper ions to the cathode if the current density is correspondingly small. No loss of efficiency would therefore result. If, however, the current be greater than the corresponding removal of the impoverished electrolyte from the cathode, the current will sieze upon the next available material in the electrolyte, and the result will be a corresponding loss of efficiency and impure and rough copper deposited. To prevent this action from taking place it is necessary to remove the film of exhausted electrolyte as rapidly as it is formed, either by violent circulation of the electrolyte, friction, or rotating cathode. Consequently the process which most effectually removes the impoverished electrolyte from the cathode, and which at the same time will give the most uniform distribution of current and the most uniform strength of electrolyte over the whole surface of the cathode, should be the one to produce the highest efficiency, the best deposits of copper, and allow of the highest current density.

Various methods are employed to accomplish these results. One generally used, is to place the electrolyzers in cascade series, that is to

say, in which there is a slight difference in level between one electrolyzer and the one next to it, so that the electrolyte pumped into a tank above the highest electrolyzer is fed into it, and gradually flows through the entire series and finally issues from the lowest in the series and is again pumped back to the tank, or to the leaching vats. The rapidity of the circulation is governed by the difference in level between any two tanks and the slant of the tank itself. If the tank has not sufficient slant, the electrolyte will overflow if the circulation is at all rapid.

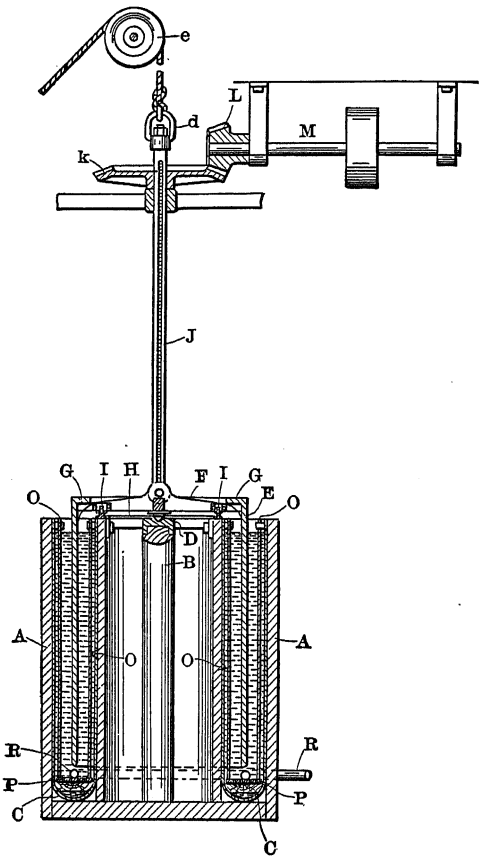


FIG. 54.—Coffin revolving cathode apparatus.

Another method of accomplishing the same purpose is to force air into the tank and electrolyte while the electrolysis is in progress. Care should be used if the electrolyte is agitated with air, that the agitation is quite uniform, in all parts of the electrolyzer. Sometimes stirrers, working reciprocally between the electrodes are used to better advantage than air, and the agitation is likely to be more uniform. The electrolyte, impinging against the cathodes in jets has given good results, but is now

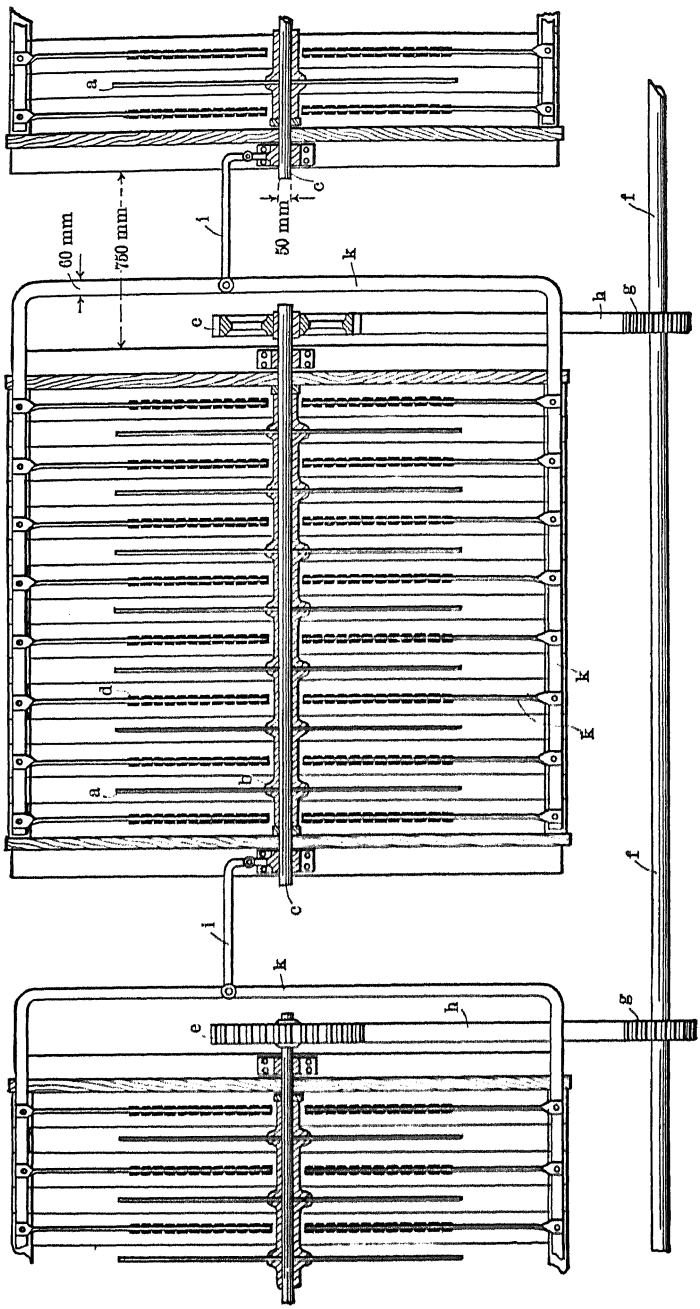


FIG. 55.—Hoepfner revolving cathode apparatus. Plan.

nowhere used. A rotating cathode gives excellent results, but a very different type of cell is required than when any of the other methods are employed. If diaphrams must be used, a rotating cathode may offer some constructional difficulties, which, however, need not be insurmountable. Fig. 54 shows one form of revolving cathode apparatus devised by Coffin[1] in which *A* is the electrolyzer, lined, preferably, with sheet lead, *B* is a post or pedestal secured in the center of the tank and surmounted by a metallic head *D*, or socket, *E* is the cathode cylinder, and *O* the anodes. Figs. 55 and 55*a* represent another form of apparatus devised by Hoepfner[2] in which *d* indicates the carbon anodes, *D* the diaphragms, and *a* the cathodes, revolving on a horizontal shaft *c*. In addition to the revolving cathode, brushes are sometimes used and adjusted so as to cause friction on the deposited cathode material. Cowper-Coles found that copper possessing the advantages of hard rolled copper of high tensile strength and free from porosity can be deposited to any thickness desired at a rapid rate by revolving the cathode at a peripheral speed of from 1500 to 2000 ft. per minute when employing current densities of 200 amperes per square foot of cathode surface and an electrolyte containing 12.5 per cent. of copper sulphate and 13 per cent. of sulphuric acid at a temperature of 40° C.[3]

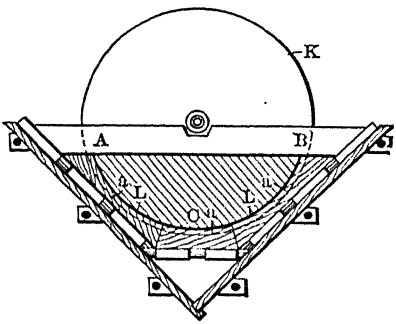


FIG. 55*a*.—Hoepfner revolving cathode apparatus Section.

In experimental work in the laboratory of applied chemistry at the University of Wisconsin[4] it was observed that the critical current density, that is to say the current density at which powdery deposit occurs, is approximately proportional to the speed of rotation, or better, to the linear feet per minute, as the cathode speed depends upon the speed of rotation and the diameter of the revolving cathode.

Betts[5] uses anodes preferably in the form of rods, and gives to them a reciprocating motion in a direction perpendicular to their length, whereby the layer of electrolyte touching the anode is rapidly changed. In electrolyzing a solution of ferrous and cupric sulphates, with a diaphragm, depositing copper on a cathode, and converting ferrous to ferric sulphate at the anode, and with a circulation of electrolyte that was previously considered amply sufficient, the electromotive force required to work the cell was considerably reduced, the evolution of gas at the

[1] U. S. Pat. 415,024, Nov. 12, 1889.
[2] U. S. Pat. 598,180, Feb. 1, 1898.
[3] U. S. Patent 895,163, Aug. 4, 1908.
[4] J. G. Zimmerman, N. Y. Meeting Electrochemical Society, 1904.
[5] U. S. Pat. 803,543 Nov. 7, 1905.

anode was entirely stopped, and the current efficiency raised from about 50 per cent. to 100 per cent. on giving the anodes a reciprocating motion of about one hundred complete cycles per minute, with an amplitude of about 1 in.

ELECTROLYTIC SULPHATE PROCESSES

The electrolytic sulphate processes may be divided into two general classes, based on the solvent, as,

Sulphuric Acid,
Ferric Sulphate,

but it is evident that neither of these processes can be carried out to the exclusion of the other. All solutions resulting from leaching roasted or oxidized ores will have more or less iron sulphate either in the ferric or ferrous condition, and the utility of a neutral solution of ferric sulphate, as compared with an acid solution, is questionable. Sulphuric acid is an energetic solvent of copper from roasted or oxidized ores, and is to be generally preferred. On certain chalcocite ores ferric sulphate has given good results without roasting.

In a copper sulphate solution containing ferrous sulphate, both sulphuric acid and ferric sulphate may be regenerated during electrolysis, and to the formation of ferric sulphate much of the difficulties in the electrolysis of impure copper sulphate solutions may be attributed. If a solution of copper sulphate, as for example that derived from leaching copper ores, is electrolyzed without a diaphragm, then in addition to the reaction;

$$CuSO_4 + H_2O + \text{Electric Current} = Cu + H_2SO_4 + O,$$

there may also take place,

$$CuSO_4 + 2FeSO_4 + \text{Electric Current} = Cu + Fe_2(SO_4)_3,$$
$$3FeSO_4 + \text{Electric Current} = Fe + Fe_2(SO_4)_3.$$

The ferric sulphate, finding its way back to the cathode, and under the influence of the current, gives rise to reversible reactions, thus:

$$Fe_2(SO_4)_3 + Cu = 2FeSO_4 + CuSO_4,$$
$$Fe_2(SO_4)_3 + Fe = 3FeSO_4,$$

thus nullifying the previous reactions, and resulting in a loss of efficiency. This loss will depend largely on the amount of iron in the solution. If the iron is excessive, the copper may be dissolved as rapidly as precipitated, and the sum total of the energy expended will be nil, so far as any useful effect is concerned.

If a suitable diaphragm is interposed between the electrodes, then both sulphuric acid and ferric sulphate are regenerated, but the deleterious reactions at the cathode are avoided, and the current efficiency may very closely approximate the theoretical, but the energy efficiency will be governed somewhat by the resistance of the diaphragm. The relative

amounts of sulphuric acid and ferric sulphate regenerated at the anode, will depend mostly on the relative proportions in the solution. If the ferrous sulphate is highly concentrated then ferric sulphate will be largely regenerated, and the process becomes one in which ferric sulphate is used as the lixiviant and in which the resulting ferrous sulphate is regenerated to the ferric sulphate.

Sulphuric Acid Process.—The simplest form of the electrolytic sulphate process is when sulphuric acid is used as the initial solvent to extract the copper from its ores and the sulphate solution thus obtained electrolyzed to deposit the copper and again liberate the combined acid. Copper in its sulphide combinations is not soluble in sulphuric acid; it is therefore necessary to roast the ore if a sulphide before the solution of the copper can be effected. After roasting, the copper will usually be in the form of oxide or sulphate, depending upon the nature of the roast. In any event, the sulphuric acid may be regarded as acting on the oxide of copper:

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

The copper sulphate so produced, in addition to that soluble in the ore, is then electrolyzed:

$$CuSO_4 + \text{Electric current} = Cu + SO_4.$$
$$SO_4 + H_2O = H_2SO_4 + O.$$

The current decomposes the copper sulphate, depositing the copper on the cathode, and the acid radical is liberated at the anode. The acid radical, combining with water, is converted into an equivalent amount of sulphuric acid to that from which the copper was deposited, and oxygen makes its appearance at the anode as a result of the secondary reaction. For every pound of copper deposited 1.54 lb. of acid is regenerated.

If there were nothing to consider but the solution of the copper from the ore with sulphuric acid, and the electrolytic decomposition of the resulting copper sulphate solution into metallic copper and the acid radical, this would be a perfect process, requiring nothing more than the expenditure of a certain amount of energy to carry it on indefinitely. The difficulties, however, in practically carrying out this simple process are considerable.

Much of the acid consumed in treating copper ores reacts with the base elements, and hence there is not sufficient acid regenerated to treat the next charge of ore; so that the deficiency has to be made up in some other way. The difficulty, therefore, of the solution of the copper is only partially solved, nevertheless it is a great step in advance of iron precipitation, where all the acid is irrecoverably lost. If the ore is a sulphide, and has to be roasted, some of this difficulty may be overcome by roasting as much of the copper as possible to sulphate rather than to oxide. The sulphate of copper thus formed is the same as that produced

by the action of sulphuric acid on copper oxide, so that while less acid is used in dissolving the copper from the ore more acid is regenerated in the electrolysis by the amount of copper soluble in the ore as sulphate. The deficiency may also be supplied by installing a small acid works in connection with the other metallurgical operations, or it may be purchased from acid manufacturers, but both of these methods add considerable to the expense, and hence do not ingeniously solve the difficulty. Further, the impurities in the ore, which cause an irrecoverable loss of acid, also contaminate the electrolyte, and cause difficulty in the electrolysis.

No really satisfactory anode for sulphate solutions has yet been discovered. Lead is ordinarily used for the insoluble anode in depositing copper from sulphate solutions, and while lead makes the best anode for sulphate solutions, it is far from being satisfactory. In depositing copper from sulphate solutions, oxygen is released at the anode; this oxygen is not entirely harmless, but attacks the lead and converts it into the peroxide, PbO_2. The peroxide, in addition to destroying the anode, offers considerable resistance to the electric current, and thus necessitates an excessive consumption of power.

In a very careful test made by Thomas P. Hughes, in Denver, to determine the peroxidation of antimonial lead anodes in electrolyzing copper sulphate solution produced by leaching Arizona carbonate ore, the following results were recorded:

Duration of test,	75.78 hours.
Copper deposited,	6.56 lb.
Average current,	30.0 amperes.
Anode area,	3.5 sq. ft.
Cathode area,	3.5 sq. ft.
Current density,	8.5 amperes per square foot.
Average voltage,	2.0 volts.
Watts,	60.0
Kilowatt-hours,	4.547
Copper per k. w.-hour,	1.4 lb.

There were 15 sheet copper cathodes, and 14 antimonial lead anodes, each 6×6 in. The anodes increased 14 oz. in weight. There was a black coating of peroxide of lead on the anodes, which could easily be scraped off. The increased weight of the anodes was evidently due to the oxygen combined with the lead to form the peroxide. As 86.6 per cent. of peroxide of lead is lead, and 13.4 per cent. oxygen, it follows that 5.6 lb. of lead was peroxidized in depositing 6.56 lb. of copper; or for every pound of copper deposited, 0.85 lb. of lead was peroxidized. The peroxide of lead, unless closely watched, is likely to drop to the bottom of the electrolyzer and short circuit the current. In this experiment the current was not operating continuously; it was turned on in the morning and shut down in the evening.

In experiments made by Greenawalt to get more information on the rate of oxidation of lead anodes, one test of 1000 ampere-hours, continuous run, with a current density of 20 amperes per square foot resulted in depositing 37 oz. of copper and in producing 14 oz. of lead peroxide. Another run of 500 ampere-hours was made in which 20 oz. of copper was deposited and 3 oz. of peroxide recovered. While still another run of 1458 ampere-hours, with a higher current density produced 60 oz. of copper and only 3 1/4 oz. of peroxide of lead.

There is no difficulty in collecting the peroxide and again reducing it to metallic lead to be reused for anodes, but it necessitates an extra expense in the operation of a plant which, however, is largely compensated for by the fact that with the exception of a small loss in reduction there is no cost for material for replacements.

The suggestion naturally occurs that if the peroxide of lead is the ultimate product of the lead anode, why not make an anode of peroxide, and thus overcome entirely the difficulties due to oxidation? This has been tried repeatedly, and Hughes tried it in various ways, but the resistance to the electric current, even with a good conducting skeleton, was so high as to put it beyond further consideration.

If sulphur dioxide is used as a depolarizer in the electrolysis of copper sulphate solutions, then, theoretically, twice the amount of acid combined with the copper is regenerated:

$$SO_4 + SO_2 + 2H_2O = 2H_2SO_4 + 21{,}320 \text{ calories},$$

but it is difficult to carry this out in practice, for the reason that the sulphur dioxide and the acid radical, at the moment of liberation, cannot be brought into sufficiently intimate contact to make it effective, especially if a reasonably large current density is used.

If sulphur dioxide is used as a depolarizer, some of the lead in the anode will be converted into the sulphate, but the action of the formation of sulphate of lead is very much slower than in the ordinary electrolysis where the lead is converted into the peroxide. The lead sulphate, however, is more difficult to reconvert back into metallic lead than the oxide.

The energy required to decompose an aqueous solution of copper sulphate is theoretically, 1.22 volts. In practice it will usually vary between 1.5 and 3 volts, depending principally upon the current density used. The theoretical output of copper is therefore, 38.35 lb. per h. p.-day, or 51.43 lb. per k. w.-day, of 24 hours. If a depolarizer is used, such for example as sulphur dioxide, then the acid radical combining with the sulphur dioxide to form sulphuric acid, will develop an electromotive force working with the current, and thus reduce the theoretical voltage, but the amount of this reduction is limited largely by the current density employed, and the completeness with which the two substances are

brought in contact with one another at the moment the acid radical is released at the anode. Tossizza[1] ascertained by experiment that the transformation of the sulphur dioxide into sulphuric acid at the anode gives rise to an electromotive force which diminishes the necessary voltage and lowers it to 0.2 volt.

While the theoretical voltage gives much desirable information, it is always best, indeed necessary, to get the voltage by direct experiment because there are so many factors which occur in practice that do not occur, and cannot be taken into account in the theoretical determinations. The practical voltage, once determined, is always constant, and is independent of the magnitude of the operation. This is a factor which can be just about as accurately determined on a small scale, on a laboratory basis, as in a large working plant. Similarly, the amount of copper deposited from a certain electrolyte, on a small scale under the conditions obtaining in practice, will always be constant, no matter what the scale of operations may be. For this reason, the factor of efficiency, and of voltage, can be quite accurately determined beforehand for any particular process and made the basis of calculations of a large plant of any sized unit.

For sulphate solutions, in practice, with a current density of 5 to 10 amperes per square foot, the voltage will usually be found to vary from 1.5 to 2.5 volts. The practical energy efficiency can only be determined by weighing the copper deposited in a certain definite time, under an observed voltage and current. It will be found, in making such tests, that frequently the results will be far from the theoretical, and that the temperature, purity of the electrolyte, and current density have much to do with the efficiency. The best that can be done in practice is to approach the theoretical efficiency although it does not follow that the most efficient process in the electrolysis is the most economical in operation.

Electrolytic Extraction of Copper From Ore at Medzianka, Poland.—At Medzianka, a copper mining locality in Russian Poland, about 50 miles from Cacrow, and 140 miles east of Breslau, explorations by the Laszczynski brothers, led to the discovery of ore bearing limestone, about 1 1/4 miles long and 150 ft. wide, containing copper ore interspersed in strips 1/2 in. thick, with calc spar and some quartz. The mineral is almost entirely copper glance, but mixed with it is a little azurite and malachite.

The produce of the mine has been divided into ore with 50 per cent. of copper which is separated underground, and mixed ore with 16 to 20 per cent. copper containing calcite and pieces of limestone, which is improved by hand picking, at the surface. The ore as brought from the

[1]U. S. Pat. 710,346, Sept. 30, 1902.

mine is crushed in rolls, mixed with 5 per cent. of damp brick earth and moulded into blocks, which when dried by the waste heat of the furnace, are subjected to a partial roasting in a kiln fired from the outside, with free access of air, which converts the copper into sulphate and oxide.

The roasted blocks are then crushed fine and leached in lead lined wooden tanks, with the electrolyzed solution from the electrolytic cells containing about 5 per cent. of free sulphuric acid. A liquor containing about 5 per cent. of copper and 1 per cent. free sulphuric acid is obtained. This solution is passed through a filter press, to thoroughly clarify it, and then electrolyzed in tanks of about 35 cu. ft. capacity. Insoluble anodes of lead plates enclosed in cloth bags, and thin copper cathodes are used. A current of 1000 amperes at 2.5 volts, corresponding to a current density of about one ampere per square decimeter of cathode surface (10 amperes per square foot) is used, producing metallic copper free from sulphuric acid or oxygen. The deposited copper, about 1.1 grm. per ampere-hour, is nearly equal to the theoretical amount. The power consumed per kilogram of copper is 2.28 k. w.-hours or 3 1/2 h. p. (1.3 k. w.-hours or 1.6 h. p.-hours per pound of copper). Between the anodes and cathodes there are wooden stirrers, which agitate the solution during the entire electrolytic process. The liquor is exhausted in from 36 to 40 hours, and then again containing about 1 per cent. copper, and from 1 to 7 per cent. free acid, is applied to a fresh lot of ore. The cathodes remain in the bath for about a month, when the deposit, from 1 to 1 1/4 in. thick, is removed and sold. It is of greater purity than the ordinary electrolytically refined copper. The four baths used in the process are served by a Siemens dynamo of 1000 amperes at 12 volts. The daily output of copper is from 225 to 500 lb. The entire process is supervised by one man in the mill without any other trained assistance.

A vital point in the success of the process is in the employment of closely fitted bags or envelopes of thick cotton duck for the lead anodes. The bags, soaked with sulphuric acid, exclude the iron salts and thus overcome much of the difficulty from that source. Its function is about the same as a diaphragm. These cotton bags are renewed about once a year.

The Laszcynski process, used at Medzianka, Russia, is described by the inventor as follows:[1]

"If a solution of sulphate of iron, $FeSO_4$, is electrolyzed, at the cathode the bivalent ferro-ion is metallically deposited at the same time the said cathion comes in contact with the insoluble anode, there being no diaphragm, and is there oxidized into trivalent ferri-ion. The latter, however, before it is deposited as metallic iron has to be reduced at the cathode to ferro-ion. In this manner there is soon set up a state of equilibrium in which the same quantity of ferro-

[1] U. S. Pat. No. 757,817, April 1, 19, 1904.

ions are reduced at the cathode as are produced at the anode. The chemical action of the current, therefore, is *nil*."

"In the present process the detrimental side action is avoided by wrapping around the insoluble anode a cover or envelope of porous fabric. The wrapping being permeable, there is before closing the circuit no difference between the chemical composition of the anode and cathode bath. As soon as the current is turned on, however, a layer of pure sulphuric acid will form around the anode, since there the SO_4 ions are discharged. Consequently new sulphuric acid is generated which can only drain off into the close-fitting envelope, displacing in this manner the solution of iron sulphate, so that in a short time a second process takes place similar to the one described. Since the ferro-ions and the ferri-ions are cathions, they travel at the closing of the circuit from the anode to cathode. The envelope around the anode forms a layer of quiet liquid, no matter if the electrolyte is in circulation, so that the traveling of the cathions can take place without being disturbed. The result of the two actions is that no ferro-ions can be oxidized, since none come in contact with the anode."

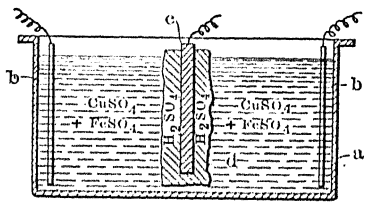


Fig. 56.

"Referring to the drawing, Fig. 56, in the application of the process to copper ores, *a* is the electrolytic cell, preferably made of wood and tightened with asphaltum or the like, *b* represents the copper sheet cathodes, and *c* represents the anode which consists of refined lead and is provided with an envelope of thick cotton stuff; for example, fustian."

All copper ores without exception contain iron, which when treated with sulphuric acid dissolves, together with the copper. By the electrolysis the iron is oxidized at the anode to ferric sulphate, which salt dissolves the copper deposited on the cathode equal to the action of dilute nitric acid:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4.$$

In this way the amount of copper deposited is not only reduced to one-half or even less, but also a brittle and inferior metal is obtained.

"The present invention now prevents the oxidation of the iron salts and makes possible the direct electrolysis of copper baths containing iron, even if they contain twice as much iron as copper, with a useful effect differing but slightly from the theoretical, because the iron remaining in the state of wholly inoffensive ferrous sulphate, $FeSO_4$, there is no corroding action of any kind."

The Laszcynski process for electrolytically obtaining metals, especially copper and zinc, out of the ores by means of insoluble anodes, consists in tightly wrapping the insoluble anode in a porous and perfectly permeable envelope, of fabric or other material, the thickness of which is in inverse proportion to the applied density of current, for the purpose of preventing anodic oxidation of the cathions.

Plant of the Intercolonial Copper Co., N. S. Canada.—The plant of the Intercolonial Copper Co., in N. S. Canada, was designed by Henry Carmichael, and according to Johnson[1] this plant for some time produced one ton of electrolytic copper daily, which was sold to brass founders as equal to the best brands of electrolytic copper.

The copper in the ore varied from 2 to 4 per cent. The very small values in the precious metals were lost. The ore was crushed to 20 mesh, which was fed by screw conveyors into a battery of 15 revolving roasters. These consisted of long tubes of cast iron passing through a firebrick muffle, heated by a flame from the fire-box. The first part of the roaster was a brick lined drum. All revolved, and the ore was first partially desulphurized in brick lined drums. It was then passed to the iron tube, where it was dead roasted. The lime was sulphated and the iron was changed to the ferric state. The roasted ore from the revolving drums was carried by a chain conveyor directly to lead lined vats of 20-tons capacity. The roasters had a capacity of 2 to 3 tons each per day.

The hot ore falling from the conveyors dropped into a 5 per cent. solution of sulphuric acid. The solution of the copper took place rapidly. The solution from the leached ore contained 2.5 per cent. copper and considerable free acid, which was drawn into a storage vat. The tailings assayed less than 0.10 per cent. copper.

The solution, as drawn from the ore and pumped to a storage tank, was impregnated with sulphur dioxide gas, made by burning brimstone in an iron pot under blast. The copper solution in the storage tank, impregnated with sulphur dioxide, was then flowed into electrolyzers, which were arranged in cascade series so that the solution could flow from one to the other. Sulphur dioxide was also blown through the electrolyte in the electrolyzers by means of perforated hard rubber tubes, which in addition to supplying the necessary sulphur dioxide, agitated the electrolyte, and thus gave the desired circulation.

The sulphur dioxide protected the lead anodes from peroxidation. The anodes were gradually converted into lead sulphate, but the sulphatization was much slower than the peroxidation which would have occurred without the introduction of the sulphur dioxide.

Large quantities of sulphuric acid were regenerated by the use of sulphur dioxide. The sulphur dioxide also acted as a depolarizer, thus reducing the necessary voltage, and consequently the amount of power, in the electrodeposition.

The copper was precipitated at the Intercolonial plant at 1.5 volts, with a current density of 6 amperes per square foot, and electrodes about 1 1/2 in. apart. The current efficiency was about 90 per cent. The

[1] *Electrochemical Industry*, April, 1903.

cathodes were greased and graphitized. The electrolysis was conducted until the copper contents was reduced from 2.5 to 1 per cent. The electrolyzed solution, regenerated in acid by the secondary anode reactions, and still containing 1 per cent. copper, was returned to the leaching vats, and the cycle continued indefinitely.

Keith Process.—In the Keith process the electrode area is increased in the different cells, as the electrolyte becomes improvished in the metal being deposited. The electrodes of each cell are in multiple in

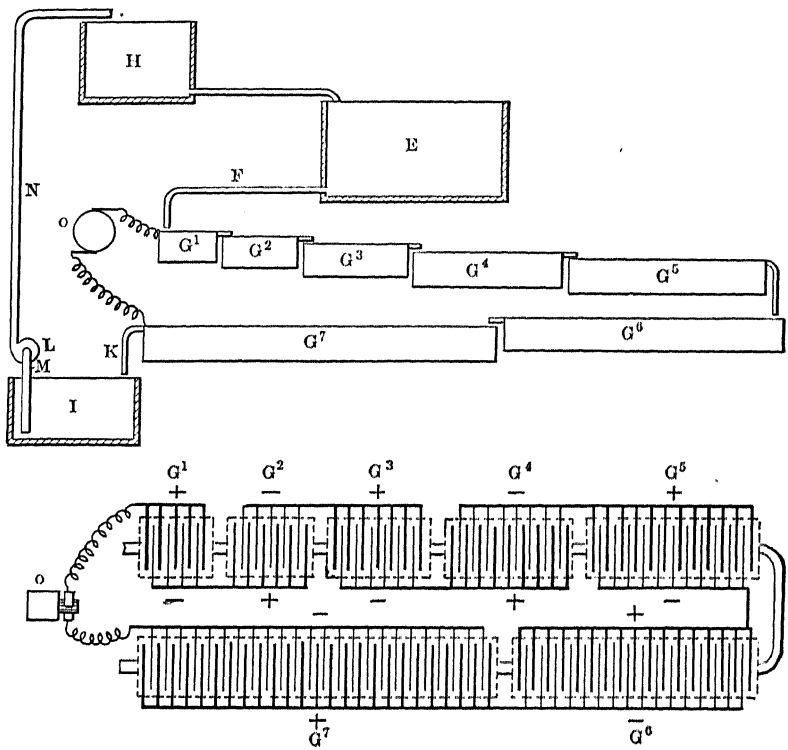


FIG. 57.—Keith process. Tanks arranged so that there is a gradual reduction of current density, as the electrolyte becomes impoverished in copper.

the cell, but in series in their relation to all other cells. The strength of current is the same in all the cells.

It is evident that a solvent, strong in the metal being deposited, entering the first cell, will admit of a greater current density in producing reguline metal on the cathodes, than will the weaker electrolyte entering the succeeding cells in the series. The deposition of metal in each cell of the series impoverishes the electrolyte which enters the succeeding cell, and therefore the current density, must be correspondingly

less in order to insure a reguline deposit of copper. To effect this Keith increases the number of electrodes, or the surface area of the electrodes, in a progressive order in each succeeding cell from the first to the last of the series so that the current density will be approximately proportional to the strength of the solution in the metals being deposited. Fig. 57.

Keith Process at Arlington, New Jersey.[1]—The ore, containing the copper as chalcocite, malachite, azurite, and cuprite, was crushed to 30 mesh, and roasted in a mechanical furnace with a hearth 200 ft. long by 10 ft. wide and fired by coal in seven fireplaces arranged along its sides. The capacity of the furnace was about 125 tons per day.

From the roasting furnace the ore was conveyed to four leaching vats, 30 ft. in diameter and 6 ft. deep, holding from 125 to 150 tons of the roasted ore. In the bottom of each tank there was a filter bed of coarsely crushed rock, covered with canvas, which was caulked tightly around the edges, and around the outlets through which the tailings were sluiced after the copper was extracted.

From the center of the bottom of each tank, under the filter bed, a pipe with a stop cock served through which to draw off the solvent to the electrolyte cells. The first solvent, consisting of sulphuric acid and largely of ferric sulphate, took up nearly all the copper and run out as cupric sulphate, and decreased in amount as the ore became improvished and the extraction completed. The tanks were then sluiced out and recharged.

The deposition vats were rectangular boxes of wood with a suitable lining. They were arranged so that the electrolyte flowed from No. 1 through the series and finally out of No. 128, depleted of its copper, into a large sump tank, from which is was pumped back into the stock tank for reuse.

The deposition vats were so set at different elevations above the floor building that the electrolyte run by gravity from one to the next, and so on through the series to the end. The vats were arranged in six rows, and one of each row at greater elevation than the end next to it of the preceding row, it was necessary to raise the electrolyte from one row to the next at those points. This was done by means of air lift pumps.

The electrical connections were as follows: the electrodes in each vat were connected in multiple, and the several vats of the electrodes connected in a series of 128. But for the purpose of insuring a retrogressive decrease of current density at the electrodes of each vat, after the first of the series, the number of electrodes was progressively increased, from the first to the last of the series. The current was the same for each vat of the series, but the current density was less and less in decremental order from the first to the last of the series, to compensate for the decrease

[1] American Inst. Electrical Eng., 1902 Meeting, S. N. Keith.

of copper in the electrolyte in its course through the vats. The current density was from 15 to 20 amperes per square foot of cathode area with a 6 per cent. copper solution, provided proper circulation and sufficiently rapid movement of the electrolyte was kept up between the anode and cathode surfaces.

During the electrolysis there was a counter-electromotive force of 1.6 volts in each of the series. The generator was operated at approximately 249 volts, which gives, for 128 cells, 1.87 per cell. The voltage, per cell, required was $1.87-1.60=0.27$ volt for resistance of conductors, etc.

Primarily both the anodes and cathodes were of sheet lead, but under electrolytic action the anodes became coated with PbO_2 and the cathodes with copper. As soon as the copper deposit reached a thickness of cardboard it was stripped off each lead cathode, which was then replaced in its cell, and the two copper sheets thus produced had connections rivited on them, and were then rehung as cathodes in some of the vats, where they remained a sufficient length of time to receive the desired thickness.

The Siemens-Halske Process.—In this process the ore is finely ground and roasted at a moderate temperature in such a way that the iron is almost completely oxidized, while the copper is contained in the roasted material, partly as copper sulphate, and partly as copper oxide, but principally as cuprous sulphide, Cu_2S. It is stated by the inventors that roasting is not necessary with all ores. The roasted ore is then treated at a temperature of about 90° C. (194° F.), with a solution of ferric sulphate, $Fe_2(SO_4)_3$, to which is added a little sulphuric acid.

On dissolving the copper, the ferric sulphate is reduced to ferrous sulphate, the copper going into solution as cupric sulphate. The solution of copper and ferrous sulphate is then led into the cathode compartment of an electrolytic cell, and in which the anodes and cathodes are separated by a permeable diaphragm. Part of the copper is deposited on the cathode, and the solution then circulates through the diaphragm to the anode. This consists of carbon rods. At the anode the ferrous sulphate is reoxidized to the ferric sulphate, which is then again used to dissolve copper from new charges of ore.

The chemical reactions, which take place during the electrolysis, and the leaching of the ore, are clearly shown by the following equations:

$$(1)\quad xH_2SO_4+2CuSO_4+4FeSO_4=2Cu+2Fe_2(SO_4)_3+xH_2SO_4,$$

in which the copper is electrolytically precipitated, and the ferrous sulphate reconverted to the ferric sulphate, at the anode. The electrolyzed and regenerated solution is then returned to the ore and the copper dissolved;

$$(2)\quad xH_2SO_4+Cu_2S+2Fe_2(SO_4)_3=2CuSO_4+4FeSO_4+S+xH_2SO_4.$$

If there is cupric oxide in the ore, it may be acted upon either by the sulphuric acid or ferric sulphate;

$$(3)\quad CuO + H_2SO_4 = CuSO_4 + H_2O.$$
$$(4)\quad 3CuO + Fe_2(SO_4)_3 = CuSO_4 + Fe_2O_3.$$

A comparison of equations 1 and 2 shows that if the copper in the ore is in the form of cuprous sulphide, the electrolyte, after passing through the leaching vats, will contain exactly the same quantity of copper sulphate, ferrous sulphate, and free sulphuric acid as it did prior to electrolysis; and that it is, therefore, completely regenerated, and may be used again for the electrolytic decomposition. But if the copper is present in the ore partly as oxide, it is evident from equations 3 and 4 that in this case the solution will be richer in copper, but poorer in respect of iron and sulphuric acid than it was before electrolysis. These equations do not take into account the possible reactions with base elements in the ore.

If a solution containing cupric and ferrous sulphates is electrolyzed in the presence of sulphuric acid, copper is deposited in preference to the iron. If the electrolysis is performed without a diaphragm between the electrodes, the ferrous sulphate is oxidized at the anode to ferric sulphate, and reduced again at the cathode to ferrous sulphate. This represents a waste of energy, which appears as heat, and the electrolyte, as a solvent for copper, is not much improved. Ferric sulphate is a solvent of copper from its oxide and sulphide combinations; ferrous sulphate is not; it is therefore desirable to have as much as possible of the iron in the solution in the ferric condition, before again applying it to the ore, and this is brought about by interposing diaphragms between the electrodes, and then passing the solution from the cathode to the anode compartment, or by permeating the solution through the diaphragm from the cathode to the anode compartment.

The scheme in the Siemens-Halske process, at first contemplated roasting the ore containing the copper sulphides, at a low temperature, so as to oxidize the sulphide of iron which it contains, to ferric oxide, and to free the cuprous sulphide originally forming a constituent of copper pyrites in the ore. In the course of the roasting some of the cuprous sulphide is converted into sulphate, but this only advances the process by the amount of copper sulphatized.

Copper-iron sulphide, as occurring in nature in the ore, is not readily soluble in ferric sulphate so that an impracticable long time is required to effect the solution of the copper, even with exceedingly fine grinding, so that a commercial application of this method of leaching sulphide ores is not feasible under existing conditions. It is impossible to perform the delicate roast necessary to release the copper sulphide and oxidize the iron sulphide.

Free copper sulphides and oxides react with ferric sulphate easily and quickly. The presence of a large quantity of ferrous sulphate in the ferric sulphate solution impairs the solution of the copper from cuprous sulphide by means of ferric sulphate.

The method suggested in the Siemens-Halske process for roasting sulphide ore, so that the main quantity of the iron is transformed to oxide while the larger portion of the copper remains as cuprous sulphide, is quite impossible. Neither can satisfactory results be obtained by dead-roasting, for the reason that at the temperature required, basic silicates are formed by means of a combination of the copper oxide with the silicates of the gangue, and perhaps also salts of the type Fe_3O_4 are formed by combination of the oxides of copper and iron; such salts are acted upon very slowly by ferric sulphate. Cuprous oxide is also formed by roasting at fairly high temperatures, and the cuprous oxide so formed is not readily soluble in a solution of ferric sulphate.

There is no difficulty in making the copper soluble by roasting at a low temperature. This temperature is about 450 to 480° C. The copper in the ore, at these temperatures, is largely converted into sulphate and some into oxide. There would appear to be no reason why the roasting should be attempted to be carried on as originally proposed by the inventors, when it is more satisfactory and just as cheap to give the ore a thorough roast at a low heat.

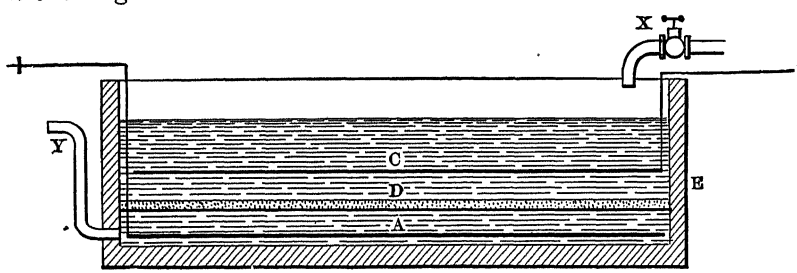


FIG. 58.—Horizontal diaphragm cell. Used in the Siemens-Halske process.

Various difficulties were encountered in the practical operation of the Siemens-Halske process, principally among these, was the indifferent nature of the solvent and the inability to obtain suitable anodes and diaphragms. The anode difficulty has not yet been overcome, as this process, in common with all other sulphate processes is still laboring under the disadvantage of not being able to find a suitable insoluble anode. In the Siemens-Halske process, as experimentally carried out some years ago, carbon was used as the anode, but it was not at all satisfactory.

In the later form of apparatus used in the electrolysis, the diaphragms and electrodes were placed horizontally, and constructed as shown in Fig. 58. The electrolyzer, *E*, is divided horizontally into two compart-

ments by an asbestos diaphragm, *D*. In the upper compartment is the cathode *C*, and in the lower compartment the anode *A*. The cathode may be made of a thin sheet of copper and the anode of carbon or of sheet lead. The solution from the ore is introduced at *K*, and drawn off at *Y*, the rate of flow being adjusted, so that it passes slowly and continuously through the permeable diaphragm *D*, and is in contact with the electrodes successively for a sufficient time to allow the deposition of most of the copper in the upper compartment, and of the oxidation of the ferrous sulphate to ferric sulphate in the lower compartment. The electrolyzed solution as withdrawn from the anode compartment is returned to the ore.

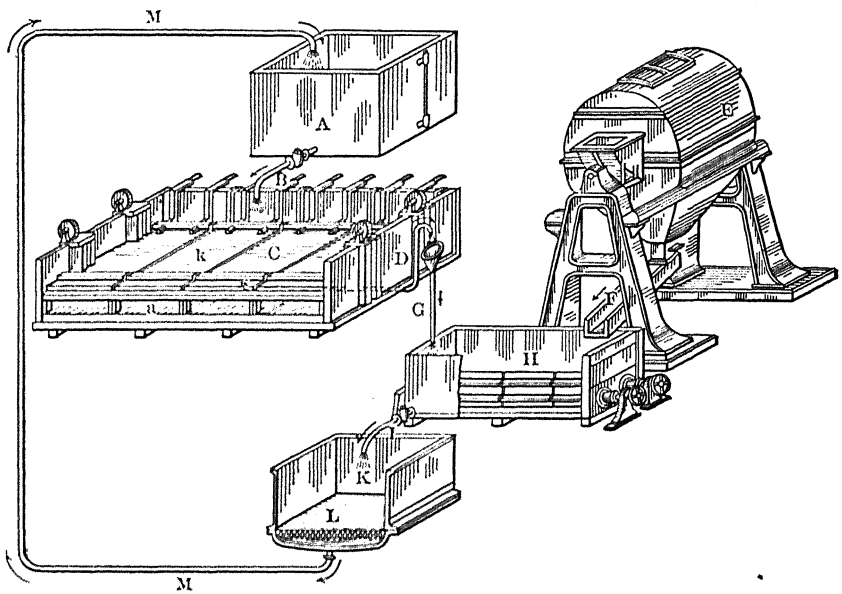


FIG. 59.—General arrangement of a Siemens-Halske plant.

Fig. 59 shows a complete outline plant for the Siemens-Halske process. *A* is the storage tank for the solution to be electrolyzed. The solution passes through the pipe *B* into the bath *C*, flows first into the cathode division *k*, and then through the filter into the anode division *a*, from which the escape pipe *D* leads it to the pipe *G*, which conducts it into the solution tank *H*. Here it comes in contact with the ore to be leached, which has been ground in the ball mill *E*. After the copper has been dissolved, the mixture of exhausted ore and liquor runs into the vacuum filter *K*. The solution aspirated through the filter is again conveyed to the storage tank *A* by the pipe *M*.

The theoretical voltage required in the Siemens-Halske process, to precipitate the copper and convert the corresponding amount of ferrous sulphate to ferric sulphate is 0.36 volt. The inventors considered that

0.7 volt would give a current density of the required strength for practical operations. In the experimental tests it varied from 0.75 to 1.8 volts. The process is nowhere now in practical use.

M. DeKay Thompson Jr.'s Experiments on the Siemens-Halske Process.

Interesting experiments on the Siemens-Halske process were made by M. DeKay Thompson Jr.[1] to determine the solvent action of ferric sulphate on copper compounds likely to occur in raw or roasted ore, and also to determine the efficiency of the electrolytic precipitation. His conclusions may be summarized as follows:

Cupric Oxide, CuO.—1. The investigation of the action of ferric sulphate on cupric oxide leads to the conclusion that the reaction between the two is probably represented by the equation:

$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3,$$

when the two are present in equivalent quantities. When this is not the case, basic salts are formed to a considerable extent.

2. Copper sulphate is precipitated by copper oxide. When the amount of oxide is equivalent to the amount of copper in the solution, the precipitation is only partial; in the presence of a large excess of copper oxide it is complete.

3. A metathesis takes place between copper oxide and ferrous sulphate, analogous to that with ferric sulphate. Ferrous oxide and copper sulphate are the resulting products.

4. Under certain conditions all iron and copper salts could be thrown out of solution.

Cuprous Oxide, Cu_2O.—1. The results of the experiments with cuprous oxide are:

1. Cuprous oxide reduces ferric sulphate to ferrous sulphate according to the equation,

$$Cu_2O + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + H_2O,$$

and both ferrous and ferric iron is precipitated.

2. Cupric sulphate does not act on cuprous oxide.

3. Ferrous sulphate does not act on cuprous oxide.

Cuprous Sulphide, Cu_2S.—The results of the experiments with cuprous sulphide showed:

1. The verification of the equation,

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S.$$

2. The $FeSO_4$ formed has no effect on cuprous sulphide.

3. The $CuSO_4$ formed has no effect on cuprous sulphide.

[1] Electrochemical Industry, June, 1904.

4. Sulphuric acid dissolves cuprous sulphide in the presence of oxygen very slowly. The presence or absence of sulphuric acid in the solvent is therefore of very little consequence as far as the Cu_2S is concerned.

Cupric Sulphide, CuS.—The following seems to be the simplest reaction that can take place between copper sulphide and ferric sulphate:

$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S.$$

In the tests some sulphur was set free, but the amount of copper dissolved was in excess of that called for by the above equation. This excess was evidently due to the oxidation of the copper sulphide to sulphate. To show this, tests were then made with sulphuric acid of 1.2 sp. gr., with a 1.15 per cent. solution of cupric sulphate, and with a 0.55 per cent. solution of ferrous sulphate. In all cases about the same amount of copper was dissolved, which shows that it was due to the oxygen present. Copper sulphide is therefore not dissolved by any of these reagents.

Many copper ores contain iron, which is changed over to oxide on roasting. The reaction that takes place between ferric oxide and ferric sulphate is to precipitate iron from the solution as a basic salt.

Experiments were then made with a copper ore having the following analysis:

Cu,	29.99 per cent.
Fe,	27.89 per cent.
S.	33.32 per cent.
SiO_2,	9.75 per cent.
	100.95 per cent.

The composition of the mineral in this ore corresponds closely to that of copper pyrites.

The first experiment showed that the ore was scarcely attacked by a 5 per cent. solution of ferric sulphate. The powdered ore, crushed to 80 mesh, was then roasted for several hours. After roasting it was found to contain 28.8 per cent. copper, and 18.9 per cent. sulphur, and the iron was computed to be 27.0 per cent. Some of the iron and copper was oxidized, so that 7.6 per cent. of the ore was copper sulphate, and 2.3 per cent. iron sulphate. Solution tests showed that not much more than 75 per cent. of the copper in this roasted ore could be dissolved from this sample with a ferric sulphate solution containing 2.833 grm. of iron in 50 c.c. of solution.

A second set of experiments were made with a smaller amount of the ore, and the same volume of solvent. In this case a little more copper was dissolved. These results confirmed those previously obtained. Experiments were then made to see if more of the copper could be dis-

solved out of the ore already treated by using fresh portions of the solvent. After from three to five treatments in this way, the ultimate extraction was 81.0 per cent. The residues from these experiments were collected and roasted again. It was found that by this means 91.8 per cent. of the copper still remaining in the ore was dissolved by the solvent in one hour.

For this reason the ore used in the above experiments was roasted again. The copper then amounted to 30.3 per cent. This ore, when agitated for 1 hour with a 6 per cent. solution of ferric sulphate showed an extraction of 93.9 per cent. of the copper. In 5 hours, under similar conditions, 98.9 per cent. of the copper was dissolved.

These experiments show that copper can be dissolved by ferric sulphate pretty completely as soon as the ore is sufficiently roasted. The question is what are the compounds formed by roasting, which are so much more soluble than the unroasted ore. It seems that this is due to the formation of copper oxide. If this is the case, just as much copper would be dissolved by sulphuric acid. To test this conclusion some of the ore was similarly treated with sulphuric acid of 1.2 sp. gr. for 5 hours. This showed an extraction of 97.7 per cent. of the copper. It was found, however, in the study of cuprous sulphide, that this was easily extracted by ferric sulphate, and this is exactly what was under investigation in these experiments, combined with sulphide of iron. It must be this double combination, therefore, that prevents the copper from being extracted by the ferric sulphate.

The results of the experiments with the ore may be summarized as follows:

1. Copper pyrites is not appreciably attacked by ferric sulphate.
2. Roasting so changes the ore that nearly all the copper can be extracted by either sulphuric acid or by ferric sulphate. This makes it seem probable that the roasting changes the copper largely over to oxide.

The Electrolysis.—The electrolysis comprises two reactions, the reduction of the copper at the cathode and the oxidation of the iron at the anode. These were investigated separately. The vessel used was a copper voltameter jar divided into three narrow compartments by two clay diaphragms made fast to the glass sides with paraffine. The anode and cathode were in the outer compartment, while the inner one prevented diffusion from one electrode to the other.

In the experiments on the deposition of copper a lead plate was used as anode, and the anode compartment was filled with sulphuric acid. The cathode compartment was filled with a solution of the following composition:

5 per cent. ferrous iron.
3.5 per cent. copper.
2.5 to 3.0 per cent. sulphuric acid

The same solution was contained in the middle compartment. During electrolysis the liquid in the cathode compartment was stirred by a current of carbon dioxide.

The object in these experiments was to determine how poor the solution may become in copper without affecting the character of the copper deposited at a given current density. This was to be determined for the different current densities. For this purpose the gain in weight of the copper cathode was compared with the copper deposited in a copper voltameter. The accompanying table gives the results obtained with a current density of 0.98 ampere per square decimeter. (9.1 amperes per square foot.)

Time in hours	Cu deposited in voltameter for 1/2 hour	Cu deposited in cell for 1/2 hour	Per cent. yield
1/2	0.3346	0.3201	98.65
1	0.3346	0.3328	99.45
1 1/2	0.3377	0.3356	99.40
2	0.3385	0.3384	100.00
2 1/2	0.3474	0.3469	99.97
3	0.3397	0.3399	100.00
3 1/2	0.3321	0.3312	99.75
4	0.3340	0.3341	100.00
4 1/2	0.3399	0.3352	

After 4 hours the copper commenced to be spongy. The cathode solution was then analyzed and was found to contain 0.72 per cent. copper. In another similar experiment with the same current density, the copper did not begin to be spongy till the strength of the solution had reached 0.38 per cent. copper.

In still another experiment with a current density of 1.8 amperes per square decimeter (16.8 amperes per square foot) the copper began to get spongy at the end of the second hour. The electrolysis was therefore discontinued and the solution in the cathode compartment analyzed. It contained 0.98 per cent. copper. The current density was then reduced to 0.47 ampere per square decimeter (4.4 amperes per square foot) and the electrolysis continued. The copper came down in good form till the concentration of copper was 0.05 per cent. in the solution. Two other experiments were carried out with current densities of 3.4 amperes and 2.6 amperes per square decimeter, respectively. (31.6 and 24.2 amperes per square foot.) In the first case the copper was deposited in a spongy form immediately. The same was true in the second case though not in so marked a manner. Some of the spongy copper was tested for iron, but this impurity was not present.

Oxidation of the Iron at the Anode.—In all of the experiments to determine the oxidation of the iron at the anode, the yield for the first

few hours amounted to more than 100 per cent. It seems probable, therefore, that if the disturbing causes were removed, the yield would not fall much below 100 per cent. At the end of the first period the solution contained 2.1 per cent. ferrous sulphate. Therefore the conclusion may be drawn that starting with a solution containing 5 per cent. ferrous iron, this may be oxidized with approximately 100 per cent. yield, till the solution contains only 2 per cent. of ferrous iron, using a current density of from 0.3 to 0.5 ampere per square decimeter (2.79 to 4.64 amperes per square foot). When the solution contains between 2 per cent. and 1 per cent. oxidizable iron, the yield would still be about 90 per cent. When the concentration is still more diminished, the evolution of gas becomes strong and the yield falls off correspondingly.

Siemens-Halske Process in Spain.—The Siemens-Halske process was installed for practical operation in Southern Tyrol in Spain, but the results were unsatisfactory, owing mostly to the indifferent nature of the solvent. The ore contained the copper in form of the compound $Cu_2S.FeS.FeS_2$, which was found difficult to dissolve, either raw or roasted, to encourage further operations. Later, the ore was roasted at a very low temperature, and leached with sulphuric acid, and the copper in the solution crystallized to copper sulphate, for which there was a good local market.

Experiments at the Ray Mines, Arizona.—W. L. Austin gives an account of experiments made at the Ray Mines, by W. Y. Westervelt in the summer of 1905, which are interesting.[1]

"Westervelt, after making preliminary wet concentration tests which gave unsatisfactory results, instituted leaching experiments on the Ray ore. These were sufficiently encouraging to warrant the construction of a small plant on the property for the purpose of carrying out further investigations.

"The ore from the Ray mines consists of disseminated sulphides in a porphyry —or schistose—gangue, and is thought to average about 2.22 per cent. copper, accompanied by little or no precious metals. Immense quantities of this ore are known to exist.

"At Ray, leaching with sulphuric acid was found to remove a small percentage of the copper from the crude ore but did not attack that which was shut up in the sulphides. However, practically all of the copper present could be readily brought into solution by treatment with a hot-acid-solution of ferric sulphate, and investigations along these lines were started in tub-lots of 200 lb. each, to determine whether or not some practical method of leaching might be developed. The process finally decided upon for experimentation at Ray was a leaching of the raw ore by ferric sulphate, the liquor being allowed to percolate through the coarse material. This was followed by treatment of the copper-bearing solution by the electric current. In the electrolytic treatment the effort was made to precipitate metallic copper, and at the same time to regenerate the liquors so that they could be reused for leaching; somewhat along the lines of the Siemens-Halske process.

[1] "Mines and Methods," Oct., 1910.

"The Ray ore was found to be very amenable to leaching, for when crushed to one-half inch size, and after the larger pieces of copper sulphide had been removed by rough jigging, a high extraction of the copper was easily effected by using ferric sulphate solution.

"Two methods of preparing the ferric sulphate were investigated: 1. Its manufacture by chemical means; and 2. through the use of electrolysis. The salt was prepared chemically by precipitating copper from sulphate solutions on scrap iron, neutralizing the ferrous liquor by means of milk of lime, and then oxidizing the emulsified ferrous hydrate by ebullition with compressed air. The ferrous hydrate produced in these operations could then be dissolved in sulphuric acid and in this manner the desired ferric sulphate obtained. Although this method of obtaining the ferric salt was feasible, it proved to be an extravagant means of reaching the desired end because of the wasteful consumption of materials.

"The second method above mentioned appears to have given more satisfactory results, but the matter was not carried far enough to have established its economic value. After considerable experimenting to determine the proper composition of solutions, density of current, and the various details of plant design, a small mill was constructed capable of treating at one time 1000 lb. of ore, and in this the complete operation was carried out, from roughly jigged ore to the leached tailings and copper cathodes. A continuous test run was made which lasted 33 days of 24 hours each.

"In the experiments all the material previously in the vats, or subsequently added, as well as the tailings resulting from the operations, were carefully sampled, weighed and assayed. The material remaining in the vats at the end of the tests was likewise treated. The same was done with the solutions in the vats, electrolytic and storage tanks.

"Commercial sulphuric acid (66° B.) was used in these experiments, and the amount added was carefully weighed, as was the water consumed. The conditions of the solutions were daily determined by assay, and at the completion of the run measurements and assays were again made.

"The electrolytic copper was deposited on cathodes previously obtained from Ray ore by deposition on, and stripping from, rolled copper sheets. The cathodes were removed and weighed daily.

"The voltage maintained at the tank was determined hourly by a Weston voltmeter, capable of being read to 0.01 volt. The amperes were determined both by hourly readings of a Weston ammeter, and by checking against the daily weighings of a standard copper voltameter.

"Closed lead pipe coils were placed in the bottom of the leaching vats for heating the charges which were kept at an average temperature of 72° C. Steam was supplied from these coils from a main line running over the five vats, the supply being regulated by a valve at each coil. Provision was made for collecting and measuring the condensed water, which amounted to 33 lb. for each pound of copper deposited. Allowance was made in calculating the results for the surface exposed to evaporation, which was excessive, and for the area exposed to condensation in such a small plant, as compared with one which might be designed for commercial purposes.

"In the Ray experiments the entire ore treated was 1 ton, the grade being

about 2.5 per cent. (50 lb. copper per ton of ore), and a total extraction of 40.28 lb. copper was effected, or 80 per cent. The tailings assayed 0.3 per cent. Five tanks were used for leaching the ore, the combined capacity being 1000 lb.

"The copper deposited per diem was 1.22 lb., or 2.44 lb. per ton of ore in the vats, and 16.4 days were required to extract 40 lb. of copper from a ton of ore. The acid consumed during the entire run was 91.4 lb., or 2.27 lb., per pound of copper deposited. The average voltage carried was 1.7 and the current consumed amounted to 22.382 ampere-hours; 0.556 ampere-hours per pound of copper produced. This is equivalent to 38.0494 kilowatt-hours for the entire run, or 0.945 per lb. of copper deposited.

"The following estimate of the cost of leaching the Ray ore was made by Mr. Westervelt, based on the erection of a sulphuric acid plant on the ground, and assuming first class ore handling facilities to be provided. It was thought that the acid could be manufactured locally for $13.00 per ton, it being understood that the cost of the sulphuric acid made at Clifton, Arizona, by the Arizona Copper Co. for use in leaching operations carried on at that place, is between $10.00 and $12.00 per ton—including the pyrites, which cost $2.00 per ton. With fuel oil at $1.25 per barrel, the use of high-pressure compound steam engines for the generation of electric current, and employing exhaust steam for heating the vats, it was estimated that the cost of producing both power and heat, including labor and fuel, would be about $0.02 per kilowatt-hour, or $130.70 per horse-power per annum.

"In the table given below neither the cost of the ore, nor interest on the capital invested, nor amortization are included in the totals. Also the expenses of shipping the product to market and of disposing it are not taken into account; in other words the figures are usually termed the operating expenses.

ESTIMATED COST OF TREATING ONE TON OF 2.5 PER CENT. ORE, AND OF PRODUCING THEREFROM 40 POUNDS OF ELECTROLYTIC COPPER IN THE FORM OF CATHODES.

	Per lb. copper	Per ton ore
Crushing and rough jigging; handling and leaching attendance,	$0.010	$0.40
Acid, 2.27 per pound of copper at $13 per ton,	0.015	0.60
Electrolytic deposition and heating vats; 0.95 k. w.-hr. per pound of copper,	0.020	0.80
	$0.045	$1.80

"In these tests the operation was carried out by allowing the liquor to percolate without employing agitation, and the material subjected to leaching was rather coarse. The result was that to extract 80 per cent. of the copper required 16.4 days, even when a temperature of 72° C. was maintained. Had the ore been crushed finer—to 1/4 in. approximately—the action would have necessarily been more rapid, and agitation would have still further decreased the time required."

According to Austin, an investigation made in 1909 as to the probable cost of handling Ray ore by wet concentration in the mill at present under construction led to the following figures:

ESTIMATED COST OF HANDLING RAY ORE

	Per ton	Per cent.
Mining,	$1.25	29.1
Transportation-Ray to Winkleman,	0.20	4.7
Milling-on basis of 5000 tons daily,	0.40	9.3
Smelting, converting, shipping East, Refining and selling,	0.93	21.7
Administration,	0.15	3.5
Total cost of treating one ton of Ray ore,	$4.29	100.0

Total cost of producing copper $0.142 per lb.

"Taking the third and fourth items (Milling, etc; Smelting, etc.) as being the nearest equivalent to cost by the wet method, showing the expense of producing electrolytic copper to be $0.045 per pound, it is evident that these amount to 31 per cent. of the probable cost of the copper, which brings the total up to $0.145 per pound, or about the equivalent of what is expected from the wet concentration mill.

"On the other hand, while the percentage of extraction accomplished by leaching was 80 per cent., that expected from wet concentration is only about 70 per cent., of which a furthur 5 per cent. of the 70 per cent. will have to be deducted for subsequent metallurgical losses before refined copper is reached."

Tosizza Process.[1]—In this process the ferruginous copper sulphate solutions are electrolyzed by introducing sulphur dioxide into the electrolyte bath, while at the same time adjusting the voltage so as to effect the decomposition of the copper while the iron remains unaffected.

Tosizza finds that the sulphur dioxide reduces the tension necessary to deposit the copper to 0.2 volt. Since copper is more readily deposited than iron, by properly regulating the voltage, copper may be deposited to the exclusion of iron. Tosizza finds this to take place between 0.2 and 0.6 volts.

Ramen Process.[2]—In order to reduce the voltage required in the decomposition of copper solutions, and have a uniform and concentrated anolyte, Ramen purposes using ferrous salts derived from precipitating a portion of the copper solution with iron. He accomplishes this by dividing the lixiviant into two parts, one part going directly to the cathode compartment of the electrolyzer, while the other part is precipitated with iron, and the ferrous liquor so obtained is passed through the anode compartment. In this way a strong ferrous solution is obtained before being brought in contact with the anode, thus acting more effectively as a depolarizer than an electrolyzed cathode solution.

[1] U. S. Patent 710,346, Sept. 30, 1902.
[2] U. S. Patent 913,430, Feb. 23, 1909.

Treatment of Ore at the Braden Copper Co's. Mine, Chile.[1]—The mines of the Braden Copper Co. are situated in the Andes mountains, O'Higgins province, Chile, 198 miles by rail from Valparaiso. The metallic minerals of the mine are iron pyrite, magnetite, chalcopyrite, bornite, and secondary chalcopyrite, in the sulphide zone; and in the zone of oxidation, limonite, cuprite, metallic copper, and the carbonates and silicates of copper. The principal non-metallic minerals, outside of the original constituents of the rock are, tourmaline, quartz, ankerite, calcite, chlorite, sericite, mica, epidote, and zircon.

The average copper content of the ore is estimated at 2.70 per cent. copper. The ore is first concentrated and an extraction of 65 per cent. is estimated in the mill concentration, and 95 per cent in the smelting. Ratio of Concentration 9 to 1. The ultimate amount of copper extracted, therefore, is estimated at 33.5 lb. per ton of ore. The concentration plant is designed for crushing with gyratory crushers and rolls, screening by means of shaking screens; treating the product on roughing and cleaning jigs of the Woodbury type, regrinding the tailings in Chilean mills, classifying the finer sizes, and treating same on Wilfly tables and Frue vanners. The concentration will be done in two separate mills, the first of three units, each unit having a nominal daily capacity of 553 tons. These two mills will be brought up to daily capacity of 3000 tons. The concentrate will be delivered either to the smelter or to the roasting plant, should leaching of the concentrate be decided on.

The average analysis of the concentrate will be about as follows;

Copper,	16 per cent	Silica,	24 per cent.
Iron,	19 per cent.	Alumina,	12 per cent.
Sulphur,	22 per cent.	Lime,	2 per cent.

A smelting plant has been designed, consisting of a blast furnace, 44×180 in. at the tuyeres, with a 7-ft. ore column, and a Pierce-Smith basic lined converter for converting the matte into blister copper.

It has also been decided to put in a leaching plant capable of treating the concentrate from one-fifth of the daily tonnage. In general, this plant will consist of roasting the concentrate, making sulphuric acid, and precipitating the copper electrolytically. Numerous experiments on a working scale have been made in America on concentrates from the Braden Copper Co., which have been most successful, and should the same success be obtained in Chile, on a much larger working scale, it is estimated that the cost of production per pound of copper will be materially reduced.

This leaching plant will consist of one Wedge furnace with acid towers and accessories, three leaching vats, three settling tanks, and

[1] Annual Report of the Company by Pope Yeatman, Consulting Engineer, *E. and M. J.*, Dec. 30, 1911.

a precipitation plant of ten tons cathode copper capacity per day, which, should leaching not be carried out, would be used for refining a certain portion of the blister copper from the blast furnace. The electrolytic precipitation plant will probably be increased so as to handle copper either from the blast furnace of from the leaching plant. What makes the method of treating the concentrate by leaching so attactive is that it is believed the costs will be lower and the extraction higher, and the basis for the low costs is the low cost of power produced by the water-power installation on the Cachapoal.

Extraction of Copper from Matte.—Copper may be extracted direct from copper matte by using the matte as an anode in an electrolyte of copper sulphate. Copper is deposited on the cathode, while the sulphur remains behind at the anode. Iron is dissolved as ferric sulphate.

It is somewhat questionable if the direct electrolysis of matte offers any advantage in practical application. Once copper is obtained as matte it is readily converted into blister copper followed by the ordinary process of electrolytic refining. If, however, conditions arise which would make advisable the extraction of copper from matte it could probably be more advantageously treated by first crushing and roasting, and then dissolving and precipitating the copper as in any other chemical or electrolytic method for the extraction of copper from ores. Marchese carried out work on a practical scale on the direct electrolysis of copper matte, and while the results were not sufficiently encouraging to warrant its continuance in practice, they are highly interesting.

Marchese Process.—In the Marchese process, as carried out on a practical scale at Stolberg, the matte was cast into anodes 31 1/2 in. square and 1 1/2 in. thick. The iron moulds in which the matte was cast were sunk in the ground so that cooling took place very slowly, thus preventing the cracking of the plates. A copper strip was cast into the anode as a positive conductor for the electric current. The cathodes consisted of copper sheets 31 1/2 in. square and 0.04 in. thick with copper strips riveted to them for suspension and conducting the current.

The average composition of the matte treated was as follows:[1]

Copper (Cu),	15 to 16 per cent.
Lead (Pb),	14 per cent.
Iron (Fe),	40 to 42 per cent.
Sulphur (S),	25 per cent.
Silver,	0.05 per cent.

The electrolyte was made by extracting the richest matte (carrying about 50 per cent. copper) with dilute sulphuric acid, and when ready for use contained about 27 to 28 grm. of copper and 15 grm. of iron per liter. The vats were arranged in cascade series, and were 7 ft. 2 in. long

[1] Borchers, *Electric Smelting and Refining*, p. 255.

by 3 ft. 3 in. wide by 3 ft. 3 in. deep, lined with lead. Each bath had 15 anodes and 16 cathodes, arranged in parallel, and at a distance of 2 in. apart.

The current density was 2.8 amperes per square foot, and the electromotive force at the begininng of the electrolysis was 1 volt per cell.

At first the electrolysis proceeded satisfactorily, but after a few days the resistance began to increase and at times reached a tension of 5 volts. The high resistance was due to a dense deposit of sulphur at the anode. Another difficulty developed in the disintegration of the anodes due to the iron and copper going into solution, so that large fragments crumbled away, filled up the space between the anodes and cathodes at the bottom of the tank, and thus short circuited the current. The deposited copper was very impure; it was found to contain antimony, bismuth, lead, iron, zinc, and sulphur. It was then determined to replace the matte with lead anodes. Under these conditions the electromotive force required was 1.7 volts, and the results at first were good, but in a short time the quantity of copper deposited fell to 60 per cent. of the theoretical and the potential rose to 2.5 volts. The immediate cause of the increase of potential was due to the formation of lead peroxide on the anode. Experiments were made with sulphur dioxide as a depolarizer, and while this did not diminish the required voltage, the yield of copper was increased and the copper was exceptionally pure, containing 99.984 Cu.

Gunther Process.[1]—In the electrolytic treatment of copper matte at Mansfeld by the Gunther Process, the matte, containing 75 per cent. copper (White metal) is cast into anodes 40 in. square and 2 in. thick, which are suspended in lead lined vats by means of T-shaped copper strips tinned on the ends, these ends being embedded in the matte. The anodes are suspended between alternate cathode plates of thin sheets of metallic copper. The anodes must be removed before they become so thin as to crumble away and contaminate the slime.

The electrolyte is heated to 75° C. by means of steam coils, and is thoroughly aerated and circulated. The electromotive force required is not more than 0.5 to 0.7 volt, and a current density of 30 amperes per square foot is used. Iron, nickel, and cobalt go into solution, small particles of the anodes (copper, silver and sulphur) collect at the bottom of the vat as slime, and the pure copper is collected on the cathodes.

To clean up the slime, the clear electrolyte is siphoned off, removed and filter pressed. It is next treated with a hot solution of acetylin tetrachloride to remove the sulphur, this sulphur separating out on cooling. The residual liquid is used again. The silver bearing mud now receives a sulphatizing roast, and is further treated by the Ziervogel method. The residue after extraction of the silver is used to neutralize that portion of the electrolyte withdrawn for purification.

[1] *E. and M. J.*, Oct. 12, 1907.

ELECTROLYTIC CHLORIDE PROCESSES

Electrolytic chloride processes may be divided into three general classes, based on the solvent:

Hydrochloric Acid,
Ferric Chloride,
Cupric Chloride,

but all of these compounds may be, and usually are, present no matter what the basis of the chloride solvent may be.

If a solution of copper chloride, containing free acid and ferrous chloride, such as might result from the leaching of copper ores, is electrolyzed without a diaphragm, then in addition to the reaction

$$CuCl = Cu + Cl$$

there will take place

$$CuCl + Cl = CuCl_2$$
$$FeCl_2 + Cl = FeCl_3.$$

The chlorine, cupric chloride, and ferric chloride, finding their way back to the cathode and under the influence of the current, give rise to the reversible reactions:

$$Cu + Cl_2 = CuCl_2$$
$$Cu + CuCl_2 = 2CuCl$$
$$Cu + FeCl_3 = CuCl + FeCl$$

thus disturbing the efficiency of the process, and the disturbance may become so great that no copper will be deposited.

If a suitable diaphragm is interposed between the electrodes, thus removing the deposited copper from the effects of the anode reactions, then a high efficiency may be obtained.

Since the reaction

$$Cu + CuCl_2 = 2CuCl$$

takes place to some extent without the intervention of the current, it is desirable to have the copper in the cuprous condition, and the iron in the ferrous state.

Under these circumstances, the electrodeposition may be highly efficient, because twice the amount of copper is deposited from the univalent cuprous chloride than from the bivalent cupric chloride, and the anode reactions give rise to an electromotive force which materially reduces the voltage necessary for the decomposition.

The resulting anode product will depend largely on the lixiviant. If the lixiviant is hydrochloric acid and the resulting copper chloride solution reasonably pure, then chlorine will be evolved at the anode. If the lixiviant is cupric chloride, as in the Hoepfner process, then with a low current density, cupric chloride will be regenerated from the cuprous chloride anolyte. Similarly, if the lixiviant is ferric chloride, as in the

Body process, then ferric chloride will be regenerated from the ferrous chloride anolyte.

The use of ferric chloride as the solvent, and its regeneration from ferrous chloride, is analogous to the corresponding ferric sulphate process.

The first attempt to use iron salts in an electrolytic copper process was made by Body, in 1886. The purely metallurgical engineering art had, up to this date, long known the utilization of iron salts, especially the oxidation, reduction, and solvent powers of its respective sulphates and chlorides. The application of these facts to the development of electrolytic methods of extracting copper from its ores, has given rise to several interesting processes. Body, in 1886, applied for a patent in which ferric chloride in connection with common salt was used as the electrolyte. This must be considered the forerunner of the Siemens-Halske process in which ferric sulphate is used as the electrolyte, and of the Hoepfner process in which cupric chloride is used as the solvent of the copper and cuprous chloride as the electrolyte.

In all processes in which the copper is dissolved as chloride either by hydrochloric acid or metal chloride, the electrodeposition is made from the cuprous, and not from the cupric chloride, although in precipitating from cuprous chloride solutions some cupric chloride may be present or formed during the electrolysis.

Electrolysis of Cupric Chloride.—When cupric chloride is electrolyzed, copper is deposited on the cathode and chlorine released at the anode. The theoretical pressure required is 1.35 volts.

$$CuCl_2 + \text{Electric current} = Cu + 2Cl$$

the chlorine released may be used in some other step in the extraction of the copper, or as a basis for the manufacture of by-products.

Experiments made in electrolyzing a solution of cupric chloride,[1] using a platinum cathode and a carbon anode, in a porous cell, showed the following interesting results:

When the solution is stirred, it is found that rapid stirring diminishes the yield for a given current, but the copper deposited is purer because the cuprous chloride formed by the dissolving of separated copper by the cupric chloride is washed away from the deposit.

In a series of experiments, the solution was circulated through the electrolytic cell and passed into another vessel containing a copper plate, and the rate at which the copper dissolved was measured. To obtain constant results the liquid must always circulate at the same rate. Addition of hydrochloric acid diminishes the current yield, but leads to a purer copper, because the cuprous chloride formed is retained in solution. When the concentration of the acid is very great the yield begins to increase slightly. Sodium chloride added to the solution diminishes

[1] *London Electrical Engineer*, 1902.

the current yield, but not to anything like the same extent as hydrochloric acid; the deposited copper is very pure. The current yield diminishes as the concentration of the cupric chloride increases, and the copper deposited becomes more impure, for more cuprous chloride is formed, and it may even happen that cuprous chloride alone is deposited. It is not advisable, however, to diminish the concentration too much, as then the copper is deposited in a very spongy form.

At a temperature of about 12° C., the deposited copper is spongy; a coherent deposit is obtained at 25° C., but as the temperature rises above this, the current yield diminishes and the deposit is not so pure.

Increase of current density slightly increases the current yield, because the solubility of the copper in the electrolyte is almost independent of this density. At very high current densities however, the current yield falls off on account of the separation of hydrogen at the cathode. A deposit containing up to 99.98 per cent. of copper can be obtained from a solution containing 0.1 gram-molecule of cupric chloride; 0.1 gram-molecule of hydrochloric acid, and 0.4 gram-molecule of sodium chloride, per liter.

Metallic copper is somewhat soluble in cupric chloride solutions, the cupric chloride being reduced to the cuprous chloride:

$$CuCl_2 + Cu = 2CuCl.$$

Metallic copper is also quite soluble in chlorine solutions, especially under the influence of the electric current and in the presence of cupric chloride.

Electrolysis of Cuprous Chloride.—When cuprous chloride is electrolyzed, copper is deposited on the cathode, and chlorine is released at the anode; but the chlorine released is only half the amount liberated in the electrolysis of cupric chloride, for the same equivalent of copper. Or it may be considered that the amount of chlorine released with a definite amount of current is the same for both the cupric and cuprous chloride, but the copper deposited from a cuprous solution is twice that deposited from a cupric solution:

$$CuCl + \text{Electric current} = Cu + Cl.$$

The chlorine liberated at the anode may escape or be used in some other step in the process. Some of it will combine with the cuprous chloride to convert it into the cupric chloride, unless proper diaphragms are interposed between the anolyte and the catholyte. If there is ferrous chloride in the electrolyte it may be converted into the ferric chloride.

$$FeCl_2 + Cl = FeCl_3.$$
$$CuCl + Cl = CuCl_2.$$

The minimum electrical pressure required theoretically to decompose cuprous chloride is 1.42 volts. Any recombination of the chlorine liberated at the anode and combining with cuprous or ferrous chloride to form the corresponding cupric and ferric salts, will tend to lower this voltage.

If diaphragms are not interposed between the anode and cathode the electrolyte will gradually be converted into the cupric chloride and the yield of copper will also gradually diminish, and if the electrolysis is continued until the solution is saturated with free chlorine, the falling off in the yield will be very perceptible.

Dr. M. DeKay Thompson, and E. R. Hamilton made some interesting investigations to determine the possible use of cuprous chloride solution to copper refining.[1] Much of this information is also interesting in connection with insoluble anodes. Dr. Thompson and Mr. Hamilton determined the conductivity of saturated solutions of cuprous chloride in solutions containing 15, 25, and 30 grm. of NaCl in 100 grm. of water. The conductivities in the following table are given in reciprocal ohms per centimeter cube.

SATURATED SOLUTIONS OF CUPROUS CHLORIDE IN SOLUTION OF

Temperature	I 15 grm. NaCl in 100 grm. water	II 25 grm. NaCl in 100 grm. water	III 30 grm. NaCl in 100 grm. water
25° C.....	0.145	0.193	0.200
40° C.....	0.185	0.245	0.258
50° C.....	0.217	0.281	0.298

As compared with the conductivity of pure sodium chloride, the saturation with cuprous chloride lowers the conductivity of the solution. For example, the conductivity at 25° of a solution made by dissolving 25 grm. of sodium chloride in 100 grm. of water is 0.225 reciprocal ohms, while after saturating it with cuprous chloride it falls to 0.145. This can be counteracted by the addition of a small amount of hydrochloric acid, which at the same time clears up the turbidity.

The measurements of the following table were made of the conductivity of a solution made by dissolving 25 grm. of sodium chloride in 100 grm. of water, saturating with cuprous chloride and adding the indicated amount of hydrochloric acid of specific gravity 1.188 at 21.7°.

Cubic centimeters of HCl added to 100 c.c. of solution	Conductivity
1.115	0.195
1.595	0.204
2.08	0.206
2.52	0.215
3.26	0.224
3.66	0.230
4.32	0 237
4.81	0.242
5.55	0.251

[1] Pittsburg Meeting Electrochemical Society, May, 1910.

For the sake of comparison measurements were also made on the conductivity of acid copper sulphate solutions. In electrolytic copper refining the solutions used in practice generally contain between 12 and 20 per cent. of crystallized copper sulphate, and between 4 and 10 per cent. free sulphuric acid, and are employed between 50° C. and 60° C. Measurements were made of two solutions: "A," containing 3.75 per cent. free acid and 12.5 per cent. copper sulphate; "B," 9.3 per cent. acid and 18.3 per cent. copper sulphate. The specific gravity of A at 22.2°, was 1.077; that of B at 21.2°, was 1.199. The results of the conductivity measurements are given in the following table:

CONDUCTIVITY OF ACID COPPER SULPHATE SOLUTIONS

Temperature	Solution A	Solution B
25° C.	0.1573	0.3260
40° C.	0.1752	0.3754
60° C.	0.1895	0.4252

As it thus appears that the conductivity of the cuprous chloride solution can be made by the addition of free hydrochloric acid as satisfactory as that of copper sulphate solutions, the next point to be investigated was the ampere-hour efficiency attainable in the electrolysis of cuprous chloride solutions.

Before studying the effect of impurities a few electrolyses were carried out in a pure solution, such as was used in the conductivity determinations. Two small cells containing a solution of 25 grm. of sodium chloride in 100 grm. of water saturated with cuprous chloride, and copper electrodes, were connected in series with a copper coulometer. The cuprous chloride cells were covered with a layer of liquid paraffine. In one cell the solution had turned to deep brown, while in the second it remained nearly white.

On electrolyzing with a current density of 2 amperes per square decimeter (18.6 amperes per square foot) at room temperature the efficiency in the dark-colored cell was 78.2 per cent., and in the other 95.9 per cent., 100 per cent. being taken as twice the amount of copper deposited in the coulometer. The anodes were eaten away badly at the surface of the liquid. This always took place in neutral solutions where there was no stirring. There was also a corresponding heavier deposit on the upper part of the cathode, as though the liquid conducted better at the top than at the bottom of the cell.

There was a great tendency to form crystalline trees of copper, so that where the current density was not uniform the tree would grow to

the anode and short-circuit the cell. Stirring the solution prevented uneven solution of tee anode and produced an even deposit on the cathode of a darker color than obtained with a sulphate solution. During the electrolysis the solution tended to oxidize and form a green scum on the surface. The scum and the turbidity of the solutions can be removed by the addition of a little hydrochloric acid.

In order to see what effect the acid has on electrolysis, to one portion of a solution of 25 grm. of sodium chloride in 100 grm. of water saturated with cuprous chloride just enough hydrochloric acid was added to clear the turbidity; to a second portion hydrochloric acid of specific gravity 1.118 was added in the proportion by volume of 4.6 of acid to 100 of solution. These were placed in cells with copper electrodes, and were connected in series with a coulometer and electrolyzed with a current density of 0.75 amperes per square decimeter (7 amperes per square foot). The cuprous chloride solutions were stirred by passing in hydrogen. The results are given in the following table:

ELECTROLYSIS OF ACID CUPROUS CHLORIDE SOLUTIONS

	Cuprous chloride		Cupric sulphate
	No. 1	No. 2	
Voltage at start	2.0	0.18	0.36
Voltage after 2 hours	3.0	0.50	0.46
Voltage after 3 hours	0.84	0.20	0.35
Gain in weight	2.68 grm.	3.05 grm.	1.66 grm.
Current efficiency	80.6 per cent.	91.6 per cent.	100. per cent.

The deposits in cells 1 and 2 were both smooth and adhered firmly. After the electrolysis the solutions stood in contact with the anodes for 48 hours. After 24 hours the first solution had a bright green scum on the surface, and had become turbid, while at the end of 48 hours the second solution had only become a little darker in color. The copper was badly corroded at the surface of the liquid in cell No. 1, while in cell No. 2 it was scarcely corroded at all.

The general results of the investigations are summed up as follows: the conductivity of cuprous chloride solution can be made as high as that of the solutions ordinarily used in copper refining, by the addition of hydrochloric acid. At room temperature a current efficiency of 90 per cent. of the theoretical can be obtained when the solutions are acidified. The presence of free acid is therefore beneficial in every respect.

The Body Process.[1]—The Body process consists essentially of separating copper, silver and gold from its ores by electrolytic action, consisting in first roasting the ore, then subjecting it to the action of ferric salt solutions, and at the same time passing an electric current through the solution, whereby the metal becomes dissolved and precipitated, and chlorine gas is generated at the positive pole, which reconverts the resulting ferrous salts into ferric salts.

In carrying out the process, the ore is first suitably ground and if a sulphide, it is roasted. The solvents employed are the ferric salts, such as ferric sulphate or ferric chloride, either alone or mixed with common salt. The ore itself is subjected to electrolytic action. The operations that take place are as follows:

1. The ores are dissolved by the action of the ferric salts, which are thereby converted into ferrous salts;

2. The dissolved copper is deposited on the cathode by the action of the current;

3. The chlorine liberated by the current at the anode effects the reconversion of the ferrous to ferric salts, and any excess of chlorine passing off, in penetrating the ore has an energetic dissolving action thereon.

Fig. 60 shows the construction of the apparatus preferred by Body to carry out the process. It is made of Portland cement, which has been found to be a good non-conductor of electricity, and which is painted inside and outside with a suitable impermeable coating. The outer walls of the apparatus are represented by *aa*, within which are inner walls, *bb*, at a small distance therefrom, and which pass down within a certain distance from the bottom surface, *c*, this being coated with a layer of carbon. The openings left below the inner walls are provided with permeable surfaces at *x*, formed of felt, and the inner surfaces of the outer walls are coated with a layer of carbon, *d*. The parts of the bottom floor between the outer and inner walls are situated at a lower level than the inner floor. The electric circuit is connected at one pole with the inner floor, and at the other pole with the two precipitating plates *XX*, suspended in the small compartments of the vessel. The solution enters at the floor, *c*, of the inner compartment, and, after flowing upward and over the tops of the inner walls, *b*, into the outer compartments, escapes through openings, *o*, near the bottom of these compartments.

By constructing the lower parts of the walls, *b*, of a permeable material the current is enabled to pass direct from the electrode, *c*, to the precipitating plates, *X*. By this arrangement the solution is subjected in the best manner to the action of the precipitating plates, and

[1] U. S. Pat. 333,815, Jan. 5, 1886.

can be made to permeate in a continuous manner through the ore. Centrally in the inner compartment is a stirrer, *e*.

A suitable solution for the treatment of the ore is 100 parts of water to 20 parts of common salt, 5 parts of persulphate of iron, and 5 parts of sulphuric acid. The solution may, however, be used without the common salt in connection with chloridized ores.

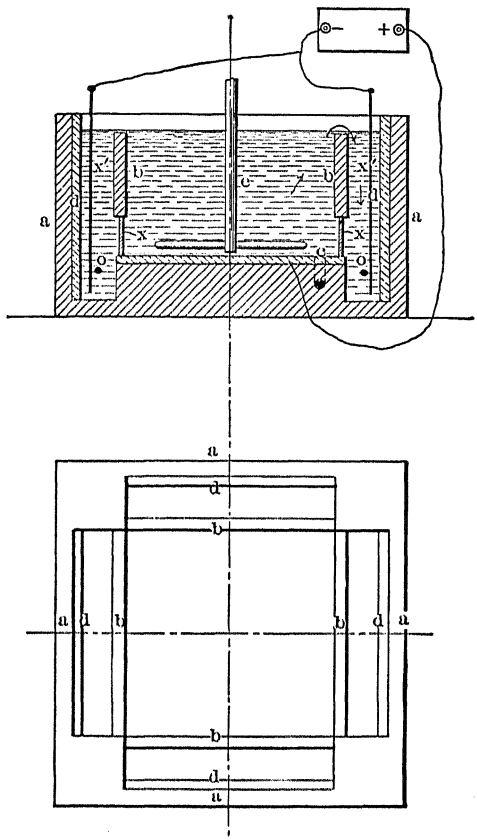


FIG. 60.—Body cell.

Body claims in his U. S. patent: "In the process of separating gold, silver, copper, and other metals from their ores by electrolytic action, the method of dissolving and precipitating the metal from the ore, and reconverting ferrous salts into ferric salt, consisting in subjecting the ore to the action of ferric salt solutions under the influence of an electric current."

This appears to be the first disclosure of the application of electrolysis to the extraction of metals from their ores, based on the reactions between ferric and ferrous chloride, and ferric and ferrous sulphate, although it is evident that Body, in his patent, preferred the chloride solution.

The Body process, although patented in Belgium as early as March, 1883, was never attempted in practice, and is chiefly of historical interest. The electrolysis of the ore direct, although frequently tried, has never met with much encouragement in any electrolytic method.

The theoretical electromotive force required in the Body process, in precipitating the ferrous from cupric chloride solution at the cathode, and reconverting the ferrous to ferric chloride at the anode, according to the following equation:

$$CuCl_2 + 2FeCl_2 = Cu + 2FeCl_3$$

is 0.15 volt. Some of the copper in the electrolyte would doubtless be in the form of cuprous chloride, and some of the chlorine released may not combine with the ferrous chloride to form ferric chloride, so that the true theoretical voltage would be quite difficult to determine.

The Hoepfner Process.—In this process cupric chloride is used as the solvent, in connection with a solution of sodium or calcium chloride. The cupric chloride reacts with the copper in the ore to form cuprous chloride, which is retained in solution by the sodium or calcium chloride. The cuprous chloride solution is then electrolyzed in a diaphragm cell, where the copper is precipitated at the cathode, and an equivalent amount of cuprous chloride is reconverted into cupric chloride, by the chlorine released at the anode. This regenerated cupric chloride solution is then again returned to the ore to dissolve more copper as cuprous chloride.

The process may be described as follows: The ore ground to about 90 mesh is automatically conveyed to leaching drums. Here it is mixed with a heated solution of cupric chloride, which contains before entering the drums 60 grm. of copper to the liter, is saturated with common salt or chloride of calcium, and is left in contact with the ore from 2 to 6 hours. Above the leaching drums is a tank filled with the necessary quantity of hot liquor to allow of continuous work.

The leaching takes place in two consecutive steps: at first in one of the drums fresh cupric chloride solution is added to the ore that has previously been treated with cupric chloride solution, to extract any remaining copper or other metals; then it is drawn into another drum containing fresh ore. Here the cupric chloride solution is completely reduced to cuprous chloride. With sulphide ores the following reactions take place:

$$CuS + CuCl_2 = Cu_2Cl_2 + S$$
$$Ag_2S + 2CuCl_2 = Cu_2Cl_2 + 2AgCl + S.$$

After all the economic metals have been extracted from the ore the residue is taken out of the drums by means of a sand pump, transferred to filter presses, washed and then dropped into cars and carried away. These tailings in careful work do not contain more than 0.2 per cent. copper.

The solution after having been completely changed to the cuprous chloride in the drums, is drawn off into vats, allowed to clear, and then purified. The purified solution now contains 120 grm. of copper (as cuprous chloride) per liter, which is twice as much as its contents before extracting the copper from the ore.

Electrolyzers are employed, which are separated by diaphragms into anode and cathode compartments, and allow an independent circulation from anode to anode, and from cathode to cathode compartments in any desirable number. In the anode compartments are placed insoluble anodes generally formed from gas retort carbon; in the cathode compartments the cathodes are of sheets of pure copper. The solution from the ore of perfectly reduced cuprous chloride in a sodium or calcium chloride solution flows into the electrolyzers in two separate streams, one going to the anodes and the other to the cathodes.

At the cathodes metallic copper is plated out at a rate of 2.36 grm. per ampere hour, exactly double the quantity as precipitated from an oxide salt of copper, such as sulphate, from which 1.18 grm. are deposited per ampere hour. At the anode, if no cuprous chloride were present, chlorine will be liberated and a potential difference of 1.8 volts will be necessary to effect the dissociation, but as cuprous chloride is always present at the anode, the chlorine ions react with the cuprous chloride and the formation of cupric chloride results:

$$Cu_2Cl_2 + 2Cl = 2CuCl_2 + 54{,}200 \text{ calories.}$$

This reaction produces an electromotive force which amounts to about one volt, and in the same direction as the working current, so that it aids the electrolytic decomposition and reduces the power necessary to plate out the copper. The electrolysis practically proceeds at a potential difference of 0.8 volt at the terminals of the cell. The solution passing the cathodes has its copper precipitated and eventually becomes free or partially free from copper. It is then withdrawn from the electrolyzers to be taken up in the cycle for the purpose of restoring the original volume of solution. The anode solution retains its original contents, but at the end of the operation the copper no longer exists as cuprous chloride, but is completely oxidized to the cupric chloride. The anode solution now containing its copper as cupric chloride, and the cathode solution, freed, or partially freed from its copper, are again mixed, so that the original condition of a cupric chloride solution containing again 60 grm. of copper per liter, is again applied to the ore.

The electromotive force required for the deposition of copper from cuprous chloride under the conditions of the Hoepfner process is, theoretically, about 0.18 volt, and practically from 0.6 to 0.8 volt. This condition, however, can only be realized at very low current densities.

The purification of the solution is accomplished by chemical means, employing copper oxide, caustic lime or alkali, whereby arsenic, antimony, and bismuth, which have a decidedly deleterious effect on the deposited copper, are removed. Silver may be either chemically removed by means of granulated copper, potassium iodide, or electrolytically, before the copper. By means of caustic lime, the iron which had been taken up is also removed. If it was not removed the iron contents of the solution would gradually increase to such an extent that the solvent ability of the impure solution would be only one-fourth that of the original solvent.

The quantity of copper precipitated by a mechanical horse-power (taking 730 volt-amperes for 24 hours at a potential difference of 0.8 volt, including 10 per cent. current loss) is approximately 43 kg. (theoretically 46.4 kg.). In view of the fact that in the larger power plants only 22 kg. of coal are required per horse-power day, we find that with economical management, 1 kg. of coal suffices to produce about 2 kg. of electrolytic copper. Taking into account 1 kg. of coal additional for grinding the ore, leaching, pumping, etc., we have the production of 1 kg. of copper to the expenditure of 1 kg. of coal.

The advantages claimed by Hoepfner for his process were:

1. The greater depositing power of the current in the cuprous solution, affording twice as much copper per hour as would be possible with a sulphate process, so that the cost of the electric installation is reduced one-half.

2. The higher efficiency of the chloride solutions, which is able to extract from the ore all the valuable metals that it contains.

3. The considerable dissolving power of the chloride solution, which may be as much as 150 grm. of copper per liter (1 1/2 lb. per gallon) in consequence of which the leaching plant may be of comparatively small size and demands the expenditure of but little mechanical power.

The hopes entertained by Hoepfner, for his process, were never realized. The process was used at the Schwartzenberger Hutte in Saxony from August, 1891, to March, 1892, and also at the Giessen an Weidenau works near Siegen. The electrolyte used consisted of cuprous chloride in calcuim chloride. Notwithstanding certain advantages the process was discontinued. The ore treated was cupriferous pyrite and phyrotite from Northern Norway. At Schwartzenberg only the richer sulphides containing 9.5 to 12.3 per cent. copper, and from 24.5 to 32.6 per cent. iron, and from 98 to 56 grm. of silver, per ton, were treated. The ore was crushed so fine that on an average 85 per cent. of any sample would pass through a sieve with 200 holes to the linear inch, and 96 per cent. would pass a 100-mesh sieve. The ore was leached in large revolving wooden barrels holding from 200 to 1500 gallons each, into which steam was admitted to hasten the reaction between the ore and the solu-

tion, the latter consisting of the cupric chloride from the anodes and calcium chloride.

The barrels gave considerable trouble owing to leakage, which increased with the rise of temperature and with the growing percentage of cuprous chloride in the solution.

The chemical reaction of a hot solution of cupric chloride on cupriferous pyrites and pyrrhotite caused a large portion of the iron to be dissolved and on this account a much higher percentage of cupric chloride had to be used in the leaching solution than would seem necessary for the ore alone. Generally 50 per cent. of the copper in the ore was obtained in the first leaching, but the remainder in the richer ores required 3 or 4 leachings, and in the poorer ores from ten to twelve leachings were required to get a satisfactory extraction on the remaining half. This unsatisfactory result was caused by the high percentages of iron in the ore, the absorption of water by the calcium chloride, and the consequent dilution of the solutions, and also by the insufficient evaporating and heating arrangements. The slimes were filter pressed after leaching in order to extract as much as possible of the solution from them. The cathodes consisted of thin copper plates of 0.25 square meter surface, and the anodes of paraffined carbon rods. The anode and cathode compartments were separated by a diaphragm of parchment enclosed in jute linen. These diaphragms were easily ruptured so that a mixture of the anode and cathode solutions frequently occurred. The carbon anodes quickly disintegrated, and the fragments of the anodes collected at the bottom of the cells, and pressing against the parchment, produced rupture.

As a result of these difficulties the daily output of copper of the plant was only 50 to 80 per cent. of the theoretical amount. The copper obtained by the Hoepfner process was of good quality in spite of the fact that it was precipitated from somewhat impure solutions. Analysis showed only traces of iron, arsenic, antimony and lead; nickel and cobalt amounting to 0.0012 per cent. and molybdenum 0.0023 per cent.

Many of the difficulties which militated against the Hoepfner process at the time these plants were in operation, would certainly not present any great impediments at the present time. The cost of fine grinding is no longer considered much of a problem, in view of the fact that immense quantities of material is ground exceedingly fine and at very low cost, in tubemills, in which the grinding is done either wet or dry. The agitation of this product with a leaching solution is also easily and cheaply accomplished. The filtering of slimes has also been worked out, but the filtering of acid copper slimes is not as easy as filtering cyanide slimes, nevertheless it should not present any very serious difficulties. Graphitized carbons have solved the practical difficulty of the anode when depositing copper from chloride solutions. Such anodes are strong and durable. Diaphragms could very likely be made of

asbestos products which would give satisfactory results. Such diaphragms are now in commercial use in enormously large plant for the electrolysis of salt into chlorine and caustic soda, where the conditions are very much more severe than in the electrolysis of cuprous chloride.

The principal difficulty appears to be metallurgical. The solution of large quantities of copper from a raw sulphide ore, with a somewhat indifferent solvent like cupric chloride, is a difficulty not easily overcome. Roasting with the present efficient mechanical furnaces is neither expensive nor difficult, and removes many of the objectionable elements from

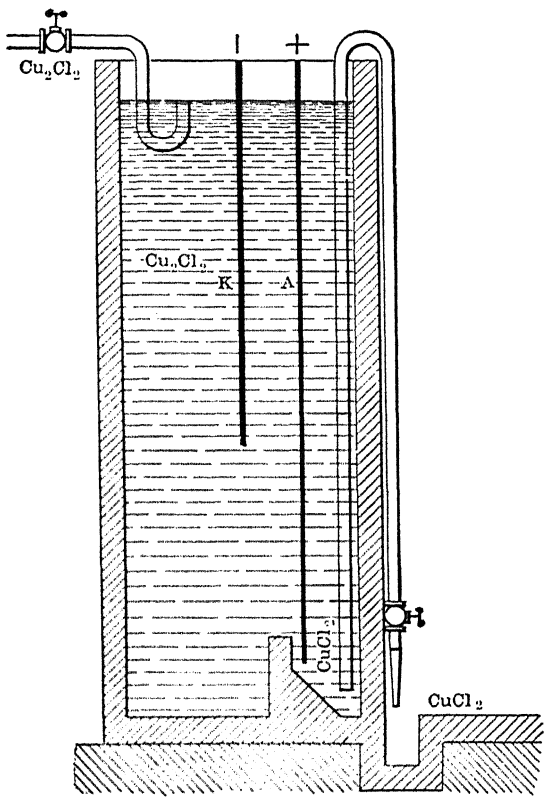


FIG. 61.—Coehn cell for electrolyzing cuprous chloride.

the ore. But even with roasted ore, it is questionable if the solvent action of cupric chloride would be sufficiently energetic to make a desirable working process.

To overcome the diaphragm difficulty in the Hoepfner process, Coehn proposed a gravity cell, which is interesting and ingenious, but under the conditions of practical copper electrolysis it is too delicate for operation and it is questionable, even with the utmost care, if it would ever lead to

working results, although it is well known that gravity cells are in successful operation in the electrolytic decomposition of salt.

The cell suggested by Cochn is shown in Fig. 61. Cochn noticed that in the electrolysis of cuprous chloride solution at a low current density that the cupric chloride produced at the anode formed a specifically heavier solution than the cuprous chloride electrolyte. On account of its greater specific weight, cupric chloride sinks to the bottom of the electrolyzer, and forms a distinct layer which constantly increases in volume, displacing the cuprous chloride electrolyte. By means of the apparatus shown in the figure the deposition of the copper was effected without the use of a diaphragm, and at a potential difference of less than one-half volt. This gives an output of approximately 74 kg. (163 lb.) per electrical horse-power day, allowing 10 per cent. loss in current.

The Douglas Process.[1]—The Douglas process consists essentially in electrolyzing solid cuprous chloride and employing the gases evolved in the treatment of copper ore and matte.

The solid cuprous chloride may be obtained from copper-bearing ores by any method, but will usually be the resultant product obtained as described in the Hunt and Douglas process, only instead of precipitating the copper from the cuprous chloride by iron or lime, Douglas precipitates the copper by electrolysis.

In the Hunt and Douglas process the ore is acted upon with sulphuric acid, producing a solution of copper sulphate; a chloride salt is then added to the copper sulphate solution, which is also subjected to the action of sulphur dioxide, when the solid cuprous chloride is formed by the following reaction:

$$2CuSO_4 + 2NaCl + SO_2 + 2H_2O = Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4.$$

The solid cuprous chloride thus thrown down is removed and placed in an electrolyzer, and both the positive and negative electrodes inserted into the solid mass. The cuprous chloride is slightly moistened with water slightly acidified, to render the electrolytic action easier. By the action of the electric current the solid cuprous chloride is converted into copper and chlorine, and by continuing the operation every trace of copper can be extracted and the chlorine can be used as a solvent of copper by bringing it in contact with moistened copper ore or matte whether the ore and matte be oxidized or not. The absorption of the chlorine or chlorine compound, by being brought in contact with the moistened ore or matte, can be effected in towers or large earthenware tubes, connected with the cells in which the cuprous chloride is electrolyzed. Fig. 62 shows the apparatus employed by Douglas in carrying out his process, in which the vessel or electrolyzer 1 is closed by the cover 2 and receives the solid cuprous chloride 3 and electrolyte 4, which

[1] U. S. Pat. No. 563,143, June 30, 1896, and No. 664,537, Dec. 25, 1900.

varies under different conditions. For instance, at one stage of the process the electrolyte may consist of solid cuprous chloride, into which the cathode is placed, and water slightly acidified with, say, hydrochloric acid, to enable it to conduct the current. As the process goes on the current deposits metallic copper and liberates chlorine and chlorine compounds, and at the end of this stage the electrolyte is a more or less acid solution of the above gases. This electrolyte may be used for leaching purposes, and when the solution so obtained is used directly as an electrolyte it will contain principally various chlorine and other compounds of copper in addition to various compounds of other metals

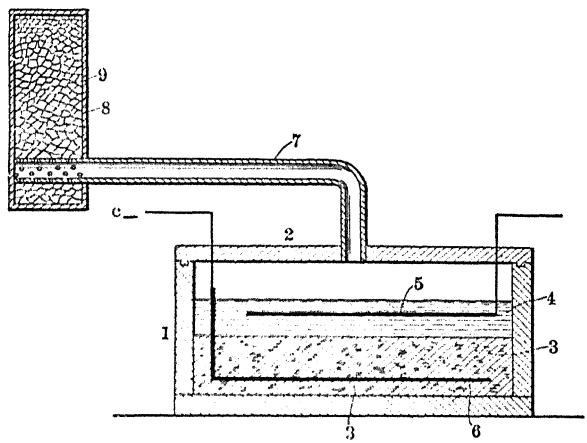


FIG. 62.—Douglas process for electrolyzing solid cuprous chloride.

present as impurities. The electrolyte, therefore, is composed of solid cuprous chloride and a solution containing acid and various compounds of copper and other metals. The anode 5 is immersed in the electrolyte and the cathode 6 is inserted in the cuprous chloride. The tower 8 is connected with the electrolyzer by means of a pipe 7. The copper ore or matte 9 is placed in the receptacle 8, and is dissolved by the chlorine or gaseous compound of chlorine evolved from the electrolytic separation of the cuprous chloride in the electrolyzer 1.

When the copper ore or matte 9 in the receptacle 8 is subjected to chlorine or gaseous compound of chlorine, the compounds of copper formed consist in part of cupric chloride, which is soluble in water, and in part of cuprous chloride, which is insoluble in water, but may be dissolved by a solution of any of the alkaline chlorides, such as chloride of sodium or chloride of calcium, or by the acid electrolyte, which, as stated, is one of the results of the electrolytic decomposition of the cuprous chloride. If the electrolyte be used to dissolve the cuprous chloride the solution may be allowed to flow back into the electrolyzer, where the copper can be deposited electrolytically.

The electrolytic recovery of the copper from the cuprous chloride, as suggested by Douglas, is unquestionably a decided step in advance of the iron or lime precipitation of the Hunt and Douglas process. Many, if not all, of the difficulties encountered by Hofmann at Argentine, Kansas, would be eliminated.

In the electrolytic precipitation of the copper from practically the pure and concentrated cuprous chloride, a high current efficiency and a high energy efficiency may be expected, and the deposited copper should be of exceptional purity.

No electrolytic difficulties could possibly develop which would be at all commensurate with the chemical difficulties the process is intended to obviate.

The Greenawalt Process.[1]—In the Greenawalt process the copper is dissolved by dilute acid chloride solutions, and then precipitated by electrolysis, while at the same time the acid, which was combined with the copper, is again regenerated and augmented, at the expense of sulphur dioxide and water. Salt is the only chemical which it is necessary to provide. Theoretically, the chlorine in the salt is not consumed; nevertheless in practice, about 1/8 lb. of salt should be provided for every pound of copper produced. The oxide, carbonate, and silicate ores of copper may be treated without roasting. The sulphides are roasted. If the ore is roasted, salt may be added during the roasting, but an oxidizing roast is preferred unless the ore contains much silver.

The ore, after being crushed, is placed in large leaching vats, or in agitators, for chemical treatment. The first step in the chemical process consists in combining chlorine, generated from metal chlorides by electrolysis, with sulphur dioxide produced by roasting concentrates or sulphide ore, in the presence of water, to form acid. This may be shown by the following well-known reactions:

$$(1)\quad 2Cl + SO_2 + 2H_2O = H_2SO_4 + 2HCl.$$
$$(2)\quad 2HCl + CuO = CuCl_2 + H_2O.$$
$$(3)\quad H_2SO_4 + CuO = CuSO_4 + H_2O.$$

Both sulphuric acid and copper sulphate react with common salt to form hydrochloric acid or cupric chloride, so that neither the sulphuric acid nor the copper sulphate could exist in the solution. These well-known reactions are:

$$(4)\quad H_2SO_4 + 2NaCl = 2HCl + Na_2SO_4.$$
$$(5)\quad CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4.$$

Cupric chloride, when warm and in the presence of other metal chlorides, acts readily on silver and its compounds in the ore to form silver chloride, thus:

$$(6)\quad Ag + CuCl_2 = AgCl + CuCl.$$

[1] *E. and M. J.*, Nov. 26, 1910. U. S. Pat. 973,776, Oct. 25, 1910.

From 80 to 90 per cent. of the silver may in this way be extracted with the copper, especially if the ore is given a chloridizing roast. If the ore contains considerable silver, it is desirable to leach with a fairly concentrated solution of base metal chlorides.

The solubility of chlorine in water is quite limited. By the indirect method of combining the chlorine with sulphur dioxide and water to form acid, any desirable strength of acid solution may be obtained for the copper, and a chlorine solution of sufficient strength for the gold.

The cupric chloride solution issuing from the leaching vats is saturated with sulphur dioxide obtained from roasting sulphide ore. This converts the cupric chloride into the cuprous chloride, thus:

$$(7)\quad 2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4.$$

The object of this is: *First*, the electric current deposits twice as much copper, theoretically, per ampere, from a cuprous as from a cupric solution, and with an expenditure of only 65 per cent. of the energy per unit of copper. *Second*, the sulphur dioxide, combining with cupric chloride and water, produces large quantities of acid. A molecule of acid is in this way regenerated for every molecule of copper reduced from the cupric to the cuprous condition. For every pound of copper reduced from the cupric to the cuprous chloride, 1.4 lb. of acid is regenerated. *Third*, the excess of sulphur dioxide combines with the chlorine liberated during the electrolysis of the cuprous chloride to precipitate the copper, thereby again regenerating 1.4 lb. of acid for every pound of copper reduced from the cuprous chloride to metallic copper. The reactions are:

$$(8)\quad 2CuCl + \text{Electric current} = 2Cu + 2Cl.$$

$$(9)\quad 2Cl + SO_2 + 2H_2O = 2HCl + H_2SO_4 + 74{,}400 \text{ calories.}$$

Fourth, the above reactions give rise to an electromotive force working with the current, thereby greatly reducing the necessary voltage in the deposition of the copper. *Fifth*, it dispenses with the necessity of diaphragms in the electrolyzers. *Sixth*, it is possible by this method to extract other valuable metals from the ore with the copper, and with the same solution. This is not possible when working on a sulphate basis. *Seventh*, insoluble anodes, precipitating metals from chloride solutions have proved vastly more durable than when precipitating from sulphate solutions. Graphitized carbon electrodes have for many years been successful both in the United States and Europe for the electrolytic decomposition of the various metal chlorides, while the production of a suitable insoluble anode for the decomposition of sulphates may still be regarded as one of the unsolved problems of electrochemistry.

It is evident that in depositing one pound of copper, 2.8 lb. of acid is regenerated at the expense of sulphur dioxide and water. This

amount of acid is capable of taking up twice the amount of copper from which it was precipitated. The regenerated acid solution is again applied to the ore, where some of the acid again combines with copper and some with the base elements, principally lime, forming the insoluble calcium sulphate, which remains in the ore. The sulphuric acid is the one which is eliminated by combining with the base elements, while the hydrochloric acid combines with the copper, again resulting in the formation of the original cupric chloride This cycle of solution, precipitation, and regeneration, is repeated indefinitely. When one vat of ore is sufficiently treated, the solution is turned into the next.

All of the metal chlorides have the faculty of displacing copper from its sulphate combinations. For example, if there is lime in the ore, as there usually is, both the sulphuric and hydrochloric acids may combine with it. If the hydrochloric acid combines with the lime, the result will be the formation of calcium chloride, but the calcium chloride will at once react with the copper sulphate in the solution and convert it into the cupric chloride, thus:

(10) $2HCl + CaO = CaCl_2 + H_2O.$
(11) $CuSO_4 + CaCl_2 = CuCl_2 + CaSO_4.$

It is evident, therefore, that the sulphuric acid is the one which is eliminated by reacting with the base elements; and the sulphuric acid resolves itself back to the sulphur dioxide from the roasting furnace.

If there is gold in the ore, the acid chloride solution is charged with chlorine, generated either from the copper chloride or from common salt, by electrolysis. It takes 1.7 lb. of salt to produce 1 lb. of chlorine, and 5 lb. of chlorine will, ordinarily, extract the gold from a ton of the average copper ore. This chlorine is not lost, but is ultimately converted into base or alkali metal chloride, in which form it is again used to extract the copper and silver from new charges of ore. Theoretically, none of the chlorine used in the process, whether free or combined, is lost. It simply changes its condition from acid to chloride in the leaching vats, and is again regenerated to acid by the electrolysis. In practice there is, of course, a small unavoidable loss of chlorine, but this should not exceed that contained in 1/8 lb. of salt per pound of copper produced.

It takes from 1/4 to 1/2 lb. of sulphur, usually in the form of sulphide ore, or concentrates, to produce 1 lb. of copper. This sulphur is used in the form of sulphur dioxide, produced from roasting the ore. After the ore is roasted, it is treated in leaching vats or agitators for the extraction of the copper. The sodium sulphate produced in the process is inert; its presence in the solution does not appear in any way to be advantageous, neither does it appear to be deleterious. It is evident that as the chlorine is not permanently taken from the cycle of operation,

the sodium sulphate formed will not accumulate indefinitely, but will be a more or less constant factor.

It will be noticed that sulphur dioxide is the substance consumed in the sulphate process, as it is also the substance consumed in the present chloride process; but the electrolytic deposition in the chloride process is from a chloride and not from a sulphate solution. In this way one of the greatest difficulties in the electrolytic extraction of copper from its ores—that of the insoluble anode—is entirely overcome.

It is intended primarily to work the process with impure solutions. Any electrolytic method, depending on pure solutions for success, must of necessity be unsatisfactory. Nevertheless, in time the solution may contain sufficiently undesirable elements to make their removal advisable. The elements most injurious to copper are bismuth, arsenic, and antimony. These, together with all the metals of the first and second groups, may be completely removed from acid solutions by hydrogen sulphide, and at the same time regenerating an amount of acid equivalent to the metals precipitated.

Should a more thorough purification be desired, the following method is preferred; Salt (NaCl) is electrolyzed to produce chlorine and caustic soda, thus:

(12) $NaCl + H_2O + \text{Electric current} = Cl + NaOH + H.$

The chlorine thus obtained is converted into acid, thus:

(13) $2Cl + SO_2 + 2H_2O + 2NaCl = 4HCl + Na_2SO_4,$

which is used to dissolve more copper from the ore. The caustic soda is used to purify the solution by precipitating out the base elements, thus:

(14) $RCl_2 + 2NaOH = 2NaCl + R(OH)_2,$

after which the purified solution, regenerated in salt, is filtered from the precipitated hydroxides.

Two kilowatt-hours, costing from 1/2 to 4 cents, will produce approximately 1 lb. of chlorine, capable of dissolving 2 lb. of copper, and 1.2 lb. of caustic soda which, at the same time, is used for the purification of the solution and regeneration of the salt. From this it will be seen that the purification of the solution is a negligible matter.

Iron cannot well accumulate in the solution in the operation of the process. Ferrous chloride is a good solvent of copper, but in dissolving the copper the iron is precipitated as the insoluble ferric oxide, and is in this way continually eliminated from the solution, thus:

(15) $2FeCl_2 + 3CuO = Fe_2O_3 + CuCl_2 + 2CuCl.$

(16) $2FeCl_2 + 3CuCO_3 = Fe_2O_3 + CuCl_2 + 2CuCl + 3CO_2.$

It will be seen from this that the iron is not only eliminated, but that the chlorine, combined with the iron, renders its equivalent in copper.

In this respect the chloride solution has an advantage over a sulphate solution, since in a chloride solution the iron is continually eliminated as the ferric oxide, while in a sulphate solution it changes from the ferric to the ferrous condition in the ore and back again in the electrolysis, but it may not be eliminated.

The iron in the chloride solution as it is applied to the ore will be in the condition of ferric chloride, and the ferric chloride is not only a good solvent of copper, but is also an excellent chloridizer of the silver which may be contained in the ore.

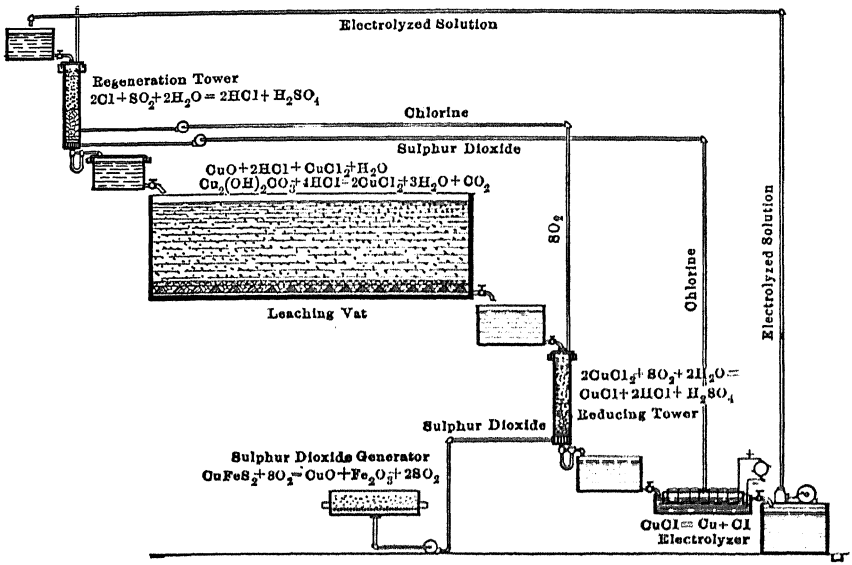


FIG. 63.—Greenawalt chloride process. Diagrammatic sketch.

The accompanying sketch, Fig. 63, shows in a general way the operation of the process, in which 1 is a leaching vat, containing the ore to be treated. An agitator would do quite as well as the leaching vat, but this point is immaterial in the operation of the process.

The acid chloride solution, coming in contact with the ore, reacts with the copper compounds, as shown by equations (2) and (3), and then issues from the vat or agitator, as a solution of cupric chloride, containing also, perhaps, some cuprous chloride, and flows into storage and regulating tank, from whence it can be passed through the reducing tower, in an even and continuous stream. The solution dripping down through the tower, while in contact with sulphur dioxide, generated in SO_2 apparatus, converts the cupric chloride into the cuprous chloride according to the reaction shown by equation (7).

The partly regenerated acid cuprous chloride solution, which will also usually contain an excess of sulphur dioxide, flows into storage and

regulating tank, from whence it is drawn into the copper electrolyze, as desired. In the electrolysis copper is deposited and chlorine liberated. Any tendency of the liberated chlorine to convert the cuprous chloride back to the cupric chloride will be immediately checked by the sulphur dioxide in the electrolyte. In working with reasonably high current densities, almost all of the chlorine will make its appearance as the gas, and is conducted by means of a pipe and exhauster, to the acid tower. The excess of sulphur dioxide from the reducing tower may also be conducted to the acid tower. The electrolyzed solution, now deprived of most of its copper, flows into a tank, where by means of pump, and pipe, it is elevated to a storage and regulating tank and from there drawn into the acid tower as desired. The solution dripping or sprayed through the acid tower, coming in contact with the chlorine from the electrolyzer, and the sulphur dioxide from the sulphur dioxide generator, reacts to form acid according to equation (1). The acid solution flows into a storage tank, where it may be drawn into the leaching vat or agitator, as desired. The original condition of things has been re-established, with the difference that an excess of acid has been regenerated. This excess is consumed by the base elements in the ore, and precludes the necessity of getting acid from extraneous sources. If the ore contains gold a chlorine solution for the extraction of the gold may be obtained by simply temporarily shutting off the sulphur dioxide from the acid tower, in which case no sulphur dioxide being present to convert the chlorine to acid, the chlorine will remain uncombined, and in solution, ready to act on the gold, or on the silver, in the ore.

Application of the Process.—The ores best adapted to the process are those which are highly silicious, preferably oxidized, and containing but little lime. Such ores are most difficult to smelt, since they contain little or no fluxing material, and usually not sufficient sulphur to form a desirable matte. The ores suited to the process may be classified as follows:

Silicious oxidized copper ores, containing the copper either as the oxide or carbonate.

Silicious sulphide ores.

Silicious copper ores containing silver, gold, or small quantities of lead.

Silicious gold and silver ores containing copper.

Copper concentrates which may contain silver, gold or lead.

If there is lime in the ore, it will not be present in the concentrates in injurious amounts. Zinc is harmful but not serious in small quantities.

Up to the present no satisfactory chemical process has yet been disclosed for the treatment of silicious gold and silver ores containing copper. It is claimed for this process that it solves the problem of the treatment of these ores. Not only is the gold and silver recovered satis-

factorily, but the copper in the ore is a benefit to the treatment, and is recovered at a profit.

The elements most injurious to an electrolytic process, and which are frequently found in copper ores, are calcium, magnesium, aluminum, and zinc. Any other elements offer no serious obstacle to the process. Of the injurious elements, the quantities which are fatal depend largely on the way they are combined in the ore. For example, calcium occurring as the sulphate, gypsum, is unaffected by the process, but calcium occurring as the oxide or carbonate, lime or limestone, is likely to give trouble if present in considerable quantities. If the ore contains much iron, roasting is desirable; if it contains sulphides, roasting is necessary.

Plants may be erected of any size and operated in any unit. For economic reasons, however, it will not ordinarily be desirable to erect and operate plants of less than 25 tons per day. For large plants a unit of 250 tons, or even 500 tons per day, will probably be the most convenient. The power consumed in the electrolysis is proportional to the amount of copper deposited.

The fineness to which it is desirable to crush the ore will depend largely on the nature of the ore. Some carbonates may be most economically treated by crushing no finer than four to eight mesh, while with sulphides it is advisable to crush to 12 or 16 mesh. If agitation is resorted to in the chemical treatment instead of percolation, the ore may be crushed to any degree of fineness desired, as now done in most plants treating gold ores by the cyanide process. The sulphur used in the process may be obtained from any source, and it may be either in the form of sulphur or of sulphide ore. Ordinarily the sulphur dioxide will be obtained from roasting sulphide ore, in which the roasting is preparatory to further metallurgical treatment.

The copper is deposited by the electric current in a granular condition and does not adhere to the cathodes. It is of exceptional purity. If carefully washed to free it from soluble salts, it will assay 99 per cent. purity before melting and casting into ingots. It is not intended by this process to make electrolytic copper direct from the ore, nevertheless, if the ore is not too complex, it is reasonably certain that copper can be produced which, after melting and fusion refining before casting into ingots, will equal in grade either Lake or Electrolytic copper. A good grade of copper can be produced from any ore.

The copper as deposited in the electrolyzer is accumulated from time to time, washed, and charged into an ordinary reverberatory melting furnace and cast into ingots, or into anodes if the copper contains sufficient silver and gold to warrant electrolytic refining. During the operation of melting it can also be refined. The copper may be withdrawn from the electrolyzers in about ten minutes. Ultimately electrolyzers will be built so that the copper may be withdrawn while they are

in operation, so that it will not be necessary to put them out of commission except for repairs. The gold and silver extracted from the ore may be deposited with the copper, or separately, if desired. If the copper needs electrolytic refining there would be no advantage in depositing the metals separately.

The percentage of extraction that may be expected will depend much on the nature of the ore. On several tons of Arizona carbonate ore, assaying 13 per cent. copper and 5.3 oz. silver per ton, the tailings assayed 0.25 per cent. copper and 0.4 oz. silver per ton, showing an extraction of 98 per cent. of the copper and 85 per cent. of the silver. On a somewhat similar ore from Utah, there was no difficulty in getting an extraction of 99 per cent. of the copper. The ore in these tests was treated raw, crushed to 4 mesh. On some pyritic concentrates from New Mexico, assaying 10.2 per cent. copper, an extraction of 90.5 per cent. was obtained in a test treating two tons of the material, crushed to 12 mesh, and roasted. A silicious sulphide ore from the San Juan district in Colorado, assaying 6.8 per cent. copper and some silver and gold, showed an extraction of 94.5 per cent. of all the metals, with the ore crushed to 16 mesh and carefully roasted.

The testing and experimental plant in Denver is capable of treating from 8 to 10 tons of ore at a time in vats holding 5 tons each. A 25-h. p. boiler and 20-h. p. engine furnish the power to drive a low voltage dynamo of 500 amperes. Two electrolyzers, each having a capacity of 500 amperes, are used to precipitate the copper. After an efficiency test the precipitated copper is carefully collected, washed to free it from soluble salts, dried and weighed to ascertain both the current and energy efficiency. A furnace having a capacity of three tons per day is used to roast sulphide ores preparatory to chemical treatment.

From such tests, covering a wide range of conditions, the basis of power consumption in the electrodeposition was obtained. One of the principal factors in these conditions was the current density, which was varied from 6.2 to 66 amperes per square foot. The average of these tests, taking good, bad, and indifferent, ranging over a period of several years, shows that a pound of copper was deposited per kilowatt-hour, and this is made the present basis of costs and power. The best tests show over 100 per cent. better than this; some as much as 2.6 lb. per kilowatt-hour. It is reasonable to suppose that with experience, and further investigation as to the cause of the principal loss of efficiency, there should be no difficulty in bringing the average up to the best yet recorded, or 2.6 lb. per kilowatt-hour. It is safer, however, to take the average efficiency until the higher efficiency is permanently established. Even the higher efficiency is only about 50 per cent. of the theoretical amount,

so there is an extremely wide margin for improvement in the saving of power from the basis of 1 lb. of copper per kilowatt-hour.

During all these tests at the Denver testing plant, the same solution was used; it was never purified, nor has any acid been added since the first test, over two years ago. The tests were made intermittently during that period. The Acheson graphite electrodes used during these tests have never been replaced and, in fact, do not show any perceptible wear. Comparative tests were made with and without diaphragms, with the result that the diaphragms have been permanently discarded.

The cost of power varies greatly in the various copper-mining districts of the world. In large installations, under ordinarily favorable conditions, there is no reason why power should not be produced for $50.00 per kilowatt-year, either with hydroelectric, gas, and possibly steam installation, assuming that for gas and steam the power is located at the railroad and the power transmitted to the reduction works. In one of the large typical hydroelectric installations in Colorado, the power costs approximately $25.00 per kilowatt-year, with an installation of several thousand kilowatts.

On a cost basis of $50.00 per kilowatt-year for the power, the cost per pound of copper for electrodeposition, on a basis of 1 pound of copper per kilowatt-hour, would be 0.58 cent, and for $25.00 per kilowatt-year it would be 0.289 cent. It is reasonably certain, however, that even these costs can be cut in half with further information on the process as to the best working conditions. In this connection it must be remembered that the power consumed also regenerates the acid, so that the cost of 0.58 cent is comparable to the combined cost of acid and iron consumed in the ordinary sulphuric acid process.

The electrolyzers are entirely automatic. No diaphragms are employed, and the cells require no further care than to remove the granular copper at stated intervals, which may vary from a day to a week, or even more. The acidity of the solution is also easily regulated. The amount of acid regenerated is at least twice that combined with the copper. Presumably the acid consumed by the matrix of the ore is a constant factor; that is to say ore containing 1 per cent. of copper will consume about the same amount of acid due to foreign substances, such as lime, as ore from the same mine having 10 per cent. copper. A 10 per cent. ore, containing 200 lb. of copper, will regenerate 560 lb. of acid, whereas a 1 per cent. ore, containing only 20 lb. of copper, will regenerate only 56 lb. of acid. It is, therefore, easy to regulate the acidity of the solution by regulating the quality of the ore, although other means are easily available.

It was clearly established in the tests in electrodeposition that the efficiency drops quite rapidly as the solution becomes impoverished in copper, and if it is too highly acid. In some of the tests the solution

showed less than 1 per cent. copper, and it was in these tests that the lowest efficiencies were obtained.

In determining the energy efficiency for any commercial plant much will depend on local conditions, especially as to the cost of power. If the power is cheap, it would be wise to drive the electrolyzers at a high current density, whereas, if the power is limited or expensive, better average results will be obtained at the lower current densities.

In the description here given, zinc has been considered as an injurious element. It is evident that the possibilities exist in the process of turning the zinc to profitable account, but as no exhaustive work has been done along this line of the process, nothing is at present claimed for it. The same is true of its application to copper-nickel ore or matte.

The approximate cost of installation and operation of extracting copper by this method, from data obtained at the Denver testing plant, is summarized below. The figures are based on a treatment of 100 tons of 5 per cent. ore (net) per day; $50.00 power cost per kilowatt year, and 1 lb. of copper deposited per kilowatt hour.

APPROXIMATE COST OF PLANT

Power installation,	$50,000
Motor-Generator set; 5000 amperes, 110 volts,	10,000
Electrolytic department; electrolyzers, cables, etc.,	25,000
Leaching department, eight 100-ton vats, pumps, etc.,	10,000
Crushing department, crushing to 6 or 8 mesh,	15,000
Miscellaneous,	10,000
	$120,000

COST OF TREATMENT

	Per ton of ore
Crushing, 8 mesh,	$0.20
Leaching,	0.15
Electrodeposition and regeneration, not including power,	0.25
Power, electrodeposition, 420 k. w.,	0.58
Repairs, renewals, etc.,	0.10
Melting and casting into ingots,	0.05
Superintendence,	0.10
Interest on investment, $120,000, at 6 per cent.,	0.20
Amortization, $120,000, at 10 per cent.,	0.33
Total cost, per ton of ore,	$1.96
Total cost, per pound of copper extracted,	1.96

If the ore is a sulphide and has to be roasted, $30,000 should be added to the cost of installation, and 75 cents per ton, to the cost of treatment, making a total cost per ton of ore treated, of $2.71, and per pound of copper extracted, 2.71 cents.

These costs include the extraction of the silver and gold, if contained in the ore, and also small quantities of lead. It does not include general

expenses of administration away from the reduction works, since such expense may be almost anything that the officers of a company may choose to make it. The copper produced is of sufficient purity to be sold direct to any consumer.

ANHYDROUS CHLORINATION PROCESSES

At certain moderately elevated temperatures, chlorine will displace sulphur quite completely from its sulphide combinations with the various metals. Processes have been based on these reactions, by electrolyzing a chloride, either in fusion or in aqueous solution, and combining the chlorine so produced, with the metals occurring as sulphides in the ore, instead of roasting. The chlorine converts the metals into chlorides, most of which are soluble in water or in a chloride solution. The metal chlorides are then dissolved from the gangue, and usually precipitated separately. The order of precipitation of metals from their chloride solutions are: platinum, gold, silver, mercury, arsenic, antimony, bismuth, copper, tin, lead, iron, zinc. By a method of substitution, therefore, it is possible to precipitate the metals, or their respective salts, separately, until finally a solution of zinc chloride is left. The chloride of zinc is then electrolyzed, either in aqueous solution, or the zinc chloride solution may be evaporated to dryness and electrolyzed in a fused condition. In either case zinc is deposited at the cathode, and chlorine released at the anode, which then again goes through the same cycle in the treatment of fresh ore.

The Swinburne-Ashcroft Process.—The first and most comprehensive process to be tried on a commercial scale, based on anhydrous chlorination, was that devised by Swinburne and Ashcroft.[1]

In the Swinburne-Ashcroft process, if there is a single sulphide, it is first treated with chlorine, so as to displace the sulphur and absorb chlorine; the chloride is then electrolyzed to get the metal and recover the chlorine. If there is a mixture of sulphides, say of zinc and of other metals, the process may be divided into three stages; the first is the treatment with chlorine, in order to change all the sulphides into chlorides; the second step is the chemical treatment of the mixed chlorides, by substitution, so that finally all the chlorine is combined with zinc; the third step is the electrolysis of the zinc chloride to extract the zinc and recover the chlorine.

If pure galena is to be smelted, it is treated with hot chlorine, so as to form lead chloride and sulphur. The sulphur is condensed as brimstone, and the lead chloride is electrolyzed in the fused state, producing lead and chlorine. If there is silver or gold present, the fused chloride of lead is treated with metallic lead. This replaces any gold or silver there

[1] James Swinburne, paper read before the Faraday Society, June 30, 1903.

may be, and the precious metals alloy with the remaining lead, so that ultimately, a bullion is produced as rich as may be desired, the only limit being its melting point which must not be too high.

The application of the process to a complex ore, containing copper, zinc, lead, etc., as the Broken Hill ore, may be described in detail. The crushed ore is run into a "transformer." This looks like a small blast furnace made of fire clay with iron outside, or of lined iron. It runs continously. When a tapping has just taken place, the transformer contains about a hundred-weight of fused chlorides and gangue. The gangue almost floats in the chlorides. If much lead is present, much of the gangue floats, so there is no caking or splitting up. The top of the transformer has a cone like a little blast furnace. Ore is poured into the fused chlorides, and at the same time chlorine is blown in. The chlorine enters at the bottom by a sort of tuyere, which is a carbon tube. The cold part of this tube is connected with iron pipe, which brings the chlorine. Dry cold chlorine is easy to handle. It does not touch metals, and iron can be freely used. The chlorine bubbling through the fused mass displaces the sulphur, which comes off and is condensed. The action of the chlorine on the sulphides evolves a great deal of heat, so that the transformer is self heating and there is no coal or coke firing, or outside heating of any sort. The temperature is controlled by the rate of admission of chlorine and ore. If the temperature is too low, chloride of sulphur may be formed. This may also be formed if there is a deficiency of ore supply. On the other hand, if the chlorine and ore are supplied too quickly, the transformer will get too hot, and some of the chlorides will distill over and be condensed with the sulphur. The temperature is the main consideration in determining the size of the transformer. It is best to have large transformers.

The pumping of dry chlorine presents no difficulty, and a chlorine pump will run day and night continuously without trouble. The dryness of the chlorine is of vital importance.

Now begins the second stage of the process. The fused mass from the transformer consists of chlorides of copper, lead, zinc, iron, manganese, silver and gangue. It is run into water and through a filter press when cool enough. This takes out the gangue and lead chloride, carrying most of the silver. The gangue is separated from the lead and silver chlorides, and these chlorides are then dried and fused in contact with lead, which extracts the silver and any gold; and then with zinc, which gives lead, practically pure, and anhydrous neutral zinc chloride, which is ready for the electrolysis vats.

The filtrate from the press contains copper, iron, manganese, and zinc. The copper is taken out as sponge or "cement copper" by zinc and there are left iron, manganese and zinc chlorides. The iron is chlorinated up to the ferric state, and zinc oxide is added to cause precipita-

tion. This throws down hydrated ferric oxide. This is the base of iron paint and is marketable, its value depending upon the color obtained. The solution is further chloridized in presence of more zinc oxide, and the manganese goes down as peroxide. Zinc has now been substituted for all the other metals in their chlorides, and nothing is left but zinc chloride.

The third step is the treatment of the zinc chloride. If it was obtained by the wet way, it is evaporated down carefully and fused. This decomposes some of the chloride and makes oxychloride. The anhydrous neutral chloride is then added to that from the lead substitution, and is taken to the final electrolysis vats.

The electrolyzers are internally heated. The cathode is fused zinc and the anode is carbon. The chlorine has no action on the carbons. The electrolyzers are kept under a slight suction, so that if there are any leaks air goes in instead of chlorine coming out. The carbons are not hot enough to be burned by this small admission of air. As the electrolyzers are kept warm by the excess of the electrical power over the chemical, the larger the cell, the lower the electromotive force. So far, 3000 amperes have been used, but this means a very small cell. The output of fused salt is enormous as compared with aqueous work. With these cells 4 volts per cell is needed; with 10,000 amperes 3 volts should do. The current efficiency is practically 100 per cent. The electrolyzers are iron-cased with fire brick; the chloride soakes into the porous brick and solidifies somewhere, so it is really a cell with zinc chloride walls.

Baker-Burwell Process.[1]—In this process the finely pulverized, practically dry ore is placed in a porcelain-lined tube mill provided with lead lined trunions, and supplied with flint pebbles. This mill is considered to be necessary for the work. The chemical action between the chlorine and metal sulphides generates so much heat that the chloride formed becomes melted, or volatilized, and spreading to the surrounding particles covers them over as by a varnish, preventing further action by chlorine. As the drum revolves, the flint pebbles grind the particles, presenting continuously fresh surfaces to be acted upon. They also tend to break up or prevent any clogging or balling of the mass. The gas is admitted to the drum, and acts at once on the ore. The metals combine with the chlorine, liberating the sulphur.

As the chemical attraction of chlorine is greater for the metals than it is for sulphur, sulphur chloride is only formed as the metal content decreases. The drum revolves during the operation, and the chlorination of the metals is effected, leaving sulphur free with the gangue, provided no heat is applied and the supply of chlorine stopped when the metals are chloridized. But if the drum be heated, sulphur chloride is formed, and at about 150° C. is expelled as a gas and may be condensed.

[1] N. Y. Meeting Electrochemical Society, Oct., 1907

If the ore treated contains gold and silver, the contents of the drum after chlorination, is emptied into leaching tanks, the soluble chlorides removed, leaving behind in the gangue with the free gold, any insoluble silver or lead chlorides remaining. In the presence of plenty of other chlorides they are both soluble, and in most cases they will be carried forward with the other solutions. During chlorination, the iron forms ferrous chloride, and gold will not become soluble in its presence, nor when chlorine is dry. The gangue, freed from all base metals and containing the free gold, is in fine condition for gold extraction. It may be recovered by wet chlorination, by cyaniding or by amalgamation in barrels. It will be too fine for plate amalgamation. Silver may be removed by leaching with sodium hyposulphite. Purification of solution follows: Granulated lead precipitates copper, granulated zinc precipitates lead. The remaining solution would then contain ferrous and zinc chlorides. Chlorine must be supplied to make the iron ferric, then zinc oxide precipitates ferric hydroxide, forming zinc chloride. Electrolysis then produces practically pure zinc, and the chlorine is liberated for use again. If the ore to be treated contains principally copper, it chloridizes as cuprous and cupric salt, either or both. If it should be cuprous it is then only partially soluble. But it is readily soluble in other chlorides, especially of sodium or calcium. Electrolysis then produces copper, liberating chlorine, the iron chloride remaining undecomposed, at the low voltage used for copper electrolysis. No deposit of copper takes place until the cathode copper becomes cuprous.

CHAPTER XIII

EXTRACTION OF PRECIOUS METALS FROM COPPER ORES

Copper ores, containing considerable value in precious metals, have not been successfully treated on a commercial scale by any hydrometallurgical process. It is true that in treating cupriferous ores, precious metals have been extracted incidentally to the process, or combination of processes, but in such cases the copper was usually considered as a deleterious element. Combinations of processes have been suggested, but these have been too expensive in practical application.

Gold and silver ores, containing only small quantities of copper, have been successfully treated by the chlorination and cyanide processes, but in such instances the copper content of the ore was small and the process worked at a disadvantage with the copper, and the copper, as such, was not profitably recovered. A successful method to treat such ores must recover all the valuable metals at a profit.

The carbonates of copper, azurite and malachite, as well as the oxides cuprite and tenorite, are attacked by cyanide with extreme rapidity, and are troublesome cyanicides. The sulphides of copper are much less readily acted upon by cyanides than are the carbonates and oxides, but they gradually dissolve. The sub-sulphide of copper, covelline, is easily attacked. The silicates are also decomposed.

The difficulties encountered in the cyanidation of cupriferous ores containing precious metals, may be summarized as follows:

1. The copper goes into solution, forming a double cyanide with the alkaline cyanide, so that beyond a certain narrow limit the consumption of cyanide becomes prohibitive.

2. The metallic copper deposited by the zinc shavings in the boxes forms a coating over the zinc which prevents the effective deposition of the gold and silver.

3. The presence of the copper in the precipitate results in a low-grade bullion which is difficult and expensive to refine.

Similarly, if the ore is treated by chlorination, the consumption of acid and chlorine is increased, and the precipitate obtained is base.

Various methods have been and may be suggested for the treatment of copper ores containing other valuable metals. These may be summarized as follows:

1. Extracting the copper from the ore with acid (or perhaps alkaline) solutions, followed by cyanidation.

2. Extracting the copper from the ore with acid solutions followed by chlorination.

3. Simultaneously extracting the copper and precious metals with or without chloridizing roasting, using an acid chloride solution containing free chlorine.

The treatment of the ore with acid for the extraction of the copper, followed by cyaniding, looks feasible enough, but the thorough washing required and the application of alkaline washes before the cyanide is applied, involves an expense which has hitherto precluded its general application, even to ores containing only a very small percentage of copper. On a laboratory scale there is no difficulty in changing a small amount of ore from acidity to the alkalinity required for successful cyaniding; in practice, on large quantities of ore, such a procedure is a serious problem. By percolation it is vastly more serious than with agitation. When large quantities of ore are treated with an acid solution in a leaching vat, it is impracticable to neutralize this acidity and bring it to the desired alkalinity. There are a number of reasons for this; among which may be mentioned the uneven percolation of the ore disintegrated by the acid solution, so that the displacing of the acid with some other solvent, or even with wash water, is difficult. Further, the acid disintegrates some of the ore, and these disintegrated compounds have an injurious effect on cyanide. Ferrous sulphate, for instance, is one of the unavoidable products of sulphuric acid leaching, and the ferrous sulphate, in the pores of the ore, is difficult to displace or to neutralize. If the ore is agitated instead of percolated, the neutralization can be more thoroughly accomplished. If the ore is agitated it will be necessary to first filter or decant the acid copper solution from the ore, then wash thoroughly to remove all the dissolved copper, and then again agitate with an alkaline solution before it is desirable to apply the cyanide. On the whole, therefore, unless the ore is quite rich in the precious metals, the extraction of the copper with an acid solution followed by a cyanide solution for the extraction of the silver and gold does not seem attractive. On the other hand, in the chlorination mills of Cripple Creek, the roasted ore is first treated with from 15 to 20 lb. of bleach and from 30 to 40 lb. of acid, per ton, after which the ore is cyanided after thorough washing. Much depends on the nature of the ore; roasted pyritic concentrates or highly silicious ore, should not offer any serious difficulty; but ores difficult to settle or difficult to filter would doubtless give trouble. It is probable that no ore containing copper as the most valuable constituent, has ever been successfully cyanided for the contained precious metals. If the copper can be extracted by an alkaline solvent, then the cyanidation of the ore for gold and silver seems more encouraging.

It is advisable in treating leached copper ores with cyanide that the

residues be thoroughly washed to remove both the acid and copper. If the acid is not thoroughly removed more alkaline material is required to neutralize the ore, and as each pound of dissolved copper combines with about 4 lb. of potassium cyanide, the consumption of cyanide will be unduly large.

Scrygmore proposed a method of cyaniding cupriferous ores, depending on the property of cupro-cyanide of potassium to dissolve copper in certain minerals. The cupro-cyanide is obtained by heating the cupriferous ore with a sufficiently dilute cyanide solution. When the cupro-cyanide solution has dissolved its maximum of copper, in the form of sub-cyanide, the excess of copper is precipitated electrolytically with regeneration of part of the cyanide. Then the ore is ready for the oridinary treatment with dilute cyanide solution.

The method proposed by Bertram Hunt depends upon the protective influence of ammonia as well as its dissolving powers for copper. The ammonia and cyanide are employed in the same solution. It is well known that the double cyanides of copper and potassium exert a solvent power for gold, but not so well known is the solubility of the cyanides of gold, silver, and copper, and other base metals in ammonia. In the treatment of cupriferous gold and silver ores by the Hunt process, the strength of solution in ammonia is varied according to the copper content, as well as the combination in which the copper is found. On material containing a few pounds of copper per ton, such as Comstock tailings, where the copper is commonly found as cupric oxide, it was found necessary to use as high as 8 lb. of caustic ammonia to the ton of solution. The strength of cyanide was 0.05 per cent. or 1 lb. to the ton. On this material, which could not be treated by ordinary cyaniding methods, the loss of cyanide was 0.06 lb. per ton. The original tailings assayed $1.45 in gold and 1 oz. in silver, and the lowest tailings after treatment showed a perfect extraction of the gold and 85.9 per cent. of the silver.

When an excess of cupric oxide is dissolved in ammonia with less cyanide that will combine with the copper, then cupric cyanide of the alkali is formed which exerts a solvent action on the gold equal to that of cyanide of potassium itself. Any salt of ammonia may be employed instead of the hydrate, provided lime or other alkali is added to the ore. Any oxidizing agent may be employed also. If the ore contains any ferrous salts these should be removed by adding to the ammonia solution an oxidizing agent previous to adding the cyanide. Atmospheric oxidation may also be used. This prevents the formation of ferrocyanide.

At Dale, San Bernardino County, California, a complex ore in which copper was present as silicate, was treated as follows: In crushing, 8 lb. of quick-lime were added per ton of ore, and in the vats the ore was treated with a 0.15 per cent. solution of potassium cyanide to which had

been added 6 lb. of ammonium chloride per ton of solution. This was allowed to remain for 12 hours in contact with the ore, after which the latter was drained and washed, the operation requiring 6 days. The filtrate was run through zinc boxes as usual. When using the ordinary cyanide solution, there was a loss of 8 lb. cyanide per ton of ore treated, while by the above method, this was reduced to 1 lb. per ton.

Cyaniding of the Cupriferous Gold Ore of the Bagdad Gold Mining Co., at Camp Rochester, in the Mohave Desert.[1]—The ore mined by this company is an altered eruptive rock, silicified, and containing iron oxide, malachite, and chrysocolla, with a gold value of $20.00 per ton and upward.

Slacked lime is added to the ore in the tanks for neutralization, and also 1 lb. of ammonium chloride for every ton of ore. The ore is then leached with a strong solution of potassium cyanide, which dissolves the copper, gold, and silver. The solution is precipitated with zinc thread, the high tenor of the solution in KCN preventing to a large extent the precipitation of the copper in the zinc boxes. The solution is then led to a tank, where the copper is precipitated with zinc dust, agitation for several hours being necessary to complete the precipitation. The amount of zinc dust required is from 1 to 1.5 times the amount of copper present in the solution.

Cyaniding of Cupriferous Gold Ore, Santa Rosa, Salvador.[2]—At the mill of the San Sebastian mine, located near Santa Rosa, Salvador, the ore is treated by cyanidation with electrolytic precipitation. The quantity of copper in the ore varies, and apparently bears no close relation to the gold content. The amount of copper extracted by the cyanide solution averages from 1.5 to 2.5 lb. per ton of ore treated.

The solutions entering the electrolytic precipitation boxes, from May 1905 to April 1906, averaged 0.089 per cent. of copper and 0.118 per cent. KCN. The solutions leaving the precipitation boxes during the same interval, averaged 0.0635 per cent. copper and 0.151 per cent. KCN. The ratio of gold to copper precipitated was 1 :9.37. 1.14 lb. of KCN was regenerated per pound of copper and gold precipitated, or 28.46 per cent. The average composition of the precipitate was: Gold 3.73 per cent.; copper, 65.0 per cent. and the remainder was lead from the cathode.

Cyanide treatment of Cupriferous Tailings, from the Cobar Chesney Mine, Cobar, N.S.W.[3]—The copper in this ore was in the form or carbonate, and the material treated was stamp mill tailings. Separate shallow rectangular wooden vats were provided for the preliminary acid treatment, each holding about 25 tons. The cyanide vats held 75 tons of

[1] C. H. Fulton, *E. and M. J.*, Jan. 13, 1906.
[2] Charles P. Richmond, *E. and M. J.*, March 16, 1907.
[3] W. S. Brown, Trans. London Institution of Mining and Metallurgy, 1906.

tailings, so that the contents of three acid vats were treated and subsequently loaded into one cyanide vat. This allowed a proper adjustment of time of treatment for continuous working and the small acid vats reduced the risk of defective treatment.

After an acid vat had been charged, 10 to 12 tons of dilute sulphuric acid were pumped on. As soon as the vat was full of solution, covering over the ore for some inches, the bottom valve was opened and the spent solution was allowed to drain off slowly through a launder to the copper precipitating boxes. When the solution had drained so as to show the ore on top of the vat, the bottom valve was again closed for about an hour and the acid allowed to remain in contact with the ore. The first solution when drained off never showed any free acid.

On again opening the bottom valve the remainder of the acid solution was allowed to percolate, usually at the rate of about 2 tons an hour, and flowed directly through the copper precipitation boxes to the sump, where it was again standardized with acid, for use on a new charge, or wasted.

The acid solution was followed immediately by a first water wash equal in weight to the original solution, which flowed into the vat from a tank above at the same rate as the vat was draining. This wash was followed by a clean water wash of about half the original quantity, and the ore was allowed to drain for discharge. The total time of acid treatment was 48 hours.

All the acid solution and wash waters passed through the copper precipitating boxes, and was either used again or run to waste depending on the supply of water available. The final wash was always clean water.

When these operations were completed and the vat ready for discharge, 0.5 to 0.8 per cent. of lime was distributed over the surface and discharged with the sands. A fairly good mixture was in this way obtained.

The acid solution was made up afresh for each vat, and its strength determined from a sample of the stamp mill tailings drawn during loading.

A portion of this sample was agitated for half an hour with a standard 1.5 per cent. sulphuric acid solution, and the consumption of acid determined by titrating with standard sodium carbonate.

The weight of acid consumed in pounds per ton of ore was then calculated, which, multiplied by the number of tons, gave the total acid required for the charge. To this an excess quantity of 25 per cent. was commonly allowed, and the weighed acid then added to the sump, well stirred, and pumped on the ore. The pump employed was a Pemberthy stream ejector, which answered extremely well. Lead piping was used.

The copper was precipitated from the solutions by passing them through two boxes, $10 \times 3 \times 4$ ft. each, divided into four compartments, as in

ordinary zinc boxes. The boxes were filled with scrap sheet iron, obtained locally in the shape of tin cans which had been burned for the recovery of the solder, and were to be had for the cost of carting.

The precipitation of the copper on the large surface of the iron thus exposed was practically perfect. On the other hand, all free acid entering the boxes was neutralized at the expense of the iron.

Before the lime was added, and the vat discharged, a second sample was drawn from the sands. On this sample a determination of cyanide consumption was made by agitating for half an hour with a 0.3 per cent. KCN solution with addition of 0.5 per cent. lime.

For some time an effort was made to determine the acidity on this sample for regulation of the quantity of lime required, but for various reasons it was found better to add 0.5 per cent. lime as a minimum. In special instances more lime was added.

No regular record was kept of the copper remaining in the residue after the acid treatment, but as a rule the extraction was almost complete. With slimes present in sufficient quantity or unevenly distributed through the sands so as to interfere with the percolation, the results were not so good.

From the acid vats the sands were trucked to the 75-ton cyanide vats for ordinary treatment. Fifteen tons of weak KCN solution were first applied to displace the approximate 15 tons brought as moisture from the acid vats. This first 15 tons carried little gold. As a rule about 12 tons would come through carrying only traces, and the other 3 tons would vary according to the relative perfection of the displacement. In many cases the first 15 tons were carefully isolated in a special sump and eventually used as a final wash for the outgoing residues. This solution was passed slowly through a zinc box, and then through about 20 cu. ft. of packed charcoal.

The zinc precipitation was not effective unless free KCN was present, showing defective displacement in the vat, in which case there would be high gold values in the solution, but when no free KCN was present and but little gold, the charcoal always caught some, if not all. If assays showed that more than a few grains of gold were still present and precipitation had been imperfect, the solution was always passed through a freshly made up zinc box, with addition of KCN, before being finally used up as a wash.

The first weak solution was allowed to drain off entirely and was then followed by a solution made up to 0.3 per cent. KCN. Several applications of this strength were made, in all between 50 and 60 tons, but between each application the sands were allowed to drain dry, the outlet being closed when a fresh lot of solution was going on.

Between 20 and 30 tons of weak solution followed, and finally 15 tons of wash.

During a trial run of 17 days 450 tons of material were treated. During this time 167.7 oz. of gold were recovered, although the actual recovery extending over a period of 9 months was 1 per cent. in excess of this.

The average value of sands treated was 9 dwt. 4 gr., of which 7 dwt. 11 gr. was recovered, leaving 1 dwt, 17 gr. in the residues, equal to an extraction of 81.1 per cent. The average theoretical strength of acid required per ton was 0.65 per cent. H_2SO_4, equal to 15.6 lb. of 92 per cent. acid.

The theoretical quantity of acid called for was 6588 lb., a difference of 1 lb. per ton coming in on correction of tonnage treated.

The quantity of acid actually consumed was 9057 lb. of 92 per cent. H_2SO_4, equal to 20.1 lb. per ton treated, or 4.5 lb. in excess of the actual requirement per ton of sands.

The copper present averaged 0.32 per cent., or equal to 144 tons for 450 tons, 7.1 lb. per ton.

The cyanide consumption was 0.072 per cent., or 1.6 lb. per ton.

From costs over several months

Scrap iron averaged 1.5d. per ton.

Lime averaged 3.6d. per ton.

Zinc averaged 2.0d. per ton.

The quantity of acid used—4.5 lb. per ton, in excess of the consumption of the ore—could have been obviated by a better arrangement. Instead of passing the acid solution direct to the copper precipitation boxes, where the excess of free acid was consumed by the iron, it might have been sent to a sump and restrengthened for a second application, or used as a preliminary wash on the next vat, and only passed through the precipitation boxes when showing no free acid. Under the circumstances in which the work was performed, it was considered economical to sacrifice acid and iron for other considerations.

The cement copper recovered averaged 60 per cent. copper; the impurities were mostly iron and silica.

No serious difficulty was found in getting a reasonable extraction of the gold from the acid treated sands. The first experiment showed a possible extraction of only 65 per cent., with 6 days' treatment, but this was found to be due to lack of aeration. While experimenting with various oxidizers it was discovered that sufficient aeration could be obtained by applying the solutions as described. In practice the solutions were well circulated in the sumps, and the usual provision made of allowing the pump suction to draw a little air.

The working solutions seldom showed over 0.3 per cent. copper, and usually were much lower. When more slimes had to be treated in the charges, conditions were not so favorable and more copper had to be dealt with in the cyanide treatment. The zinc boxes

then required careful attention, and the endeavor was to get as clean a precipitation of copper, as well as of gold, as possible. Lead acetate was freely used and the boxes freshly made up at close intervals. No cyanide solutions were at any time discarded. When the solutions were foul they were always high in gold contents, and as the precipitation of gold was accompanied by the precipitation of the copper, re-aeration restored their working usefulness.

The product of the zinc boxes was extremely base, both from the copper precipitated and the lead employed to assist that precipitation. In the clean-up after solution and removal of zinc by sulphuric acid, and careful washing with distilled water, nitric acid was used to remove the copper and lead. This latter operation had to be performed with considerable care to avoid getting gold into solution.

All solutions employed in the clean-up, including washes, were decanted into storage tanks and held until their values had been determined by assay. By using distilled water throughout and precipitating any chlorides with silver, no difficulty was experienced in producing bullion over 900 fine without loss. The ore itself carried very little silver.

Extraction of the Precious Metals with Chloride Solutions.— If the copper is extracted with an acid solution, the most logical way of recovering the gold is with chlorine, and the most logical way of extracting the silver, is with a chloride solution.

After the ore has been treated with an acid solution to dissolve the copper, it is in excellent condition for the application of chlorine, since chlorine itself is in the nature of an acid element. If the acid solution used is hydrochloric, there is no reason why the chlorine cannot be used with the copper extracting solution. If sulphuric acid is used as the solvent for the copper, it would be necessary to chlorinate the ore for the gold with a separate solution, for, if chlorine is used in connection with sulphuric acid, the dissolved copper would be converted into cupric chloride, and the treatment would then, in effect, become a chloride process. Therefore, if a cupriferous gold ore is treated with sulphuric acid to extract the copper, the chlorine treatment must follow the sulphuric acid treatment; if the ore is treated with hydrochloric acid, the chlorine treatment may follow the hydrochloric acid treatment, or be used more or less in connection with it.

Silver, in paying quantities, is more generally associated with copper ores than is gold. The extraction of the silver offers a more serious problem. Silver is not soluble in a sulphate solution; hence if a sulphate solution is employed to extract the copper, some other means must be provided to extract the silver. This, then, would involve two processes for the extraction of the copper and the silver. The silver, before it can be dissolved, must be converted into the chloride, but the chloride of silver, once formed, is quite insoluble in most solutions. Sodium

thiosulphate is an excellent solvent of silver chloride, but the same objections apply to the use of that chemical as apply to cyanide, in that it is in the nature of an alkaline or neutral solvent and is decomposed by acids.

If the copper ore contains considerable amounts of silver, which is not usually the case, a preliminary chloridizing roasting might be advisable, but chloridizing roasting is expensive and loss by volatilization must be taken into consideration. Ores, however, which contain sufficient silver to make chloridizing roasting advisable, would be more properly characterized as argentiferous than cupriferous.

If the silver in the ore is not excessive there will usually be no trouble in extracting it with the copper, by using a chloride solution. If the silver is to be extracted with a chloride solution it will be necessary to first convert the silver into the chloride, and then provide a suitable solvent for the silver chloride.

Silver and many of its compounds are converted into the chloride by cupric chloride, which may always be abundant in the copper solution. Karsten found that at temperatures ranging from 12° to 20° C. (53.6 to 68.0° F.) the action took place very slowly without, and very rapidly with, the presence of sodium chloride.

$$CuCl_2 + 2Ag = CuCl + AgCl.$$

In leaching copper ores with a chloride solution, ferric chloride is invariably present. Ferric chloride, like cupric chloride, has the faculty of converting silver and its compounds into chloride of silver.

$$FeCl_3 + Ag = FeCl_2 + AgCl.$$

Wetzler states that when a dilute solution of ferric chloride is poured upon silver leaf the latter almost instantaneously loses its luster and falls into small spangle-like flakes, of which the powder is black with a slight brown tinge. This product is the black chloride of silver, and Wetzler considered it to be a sub-chloride, identical with that resulting from the action of sunlight on ordinary silver chloride. By the action of sodium chloride it is converted into metallic silver, and chloride of silver, which dissolves.

Silver sulphide is soluble in both cupric and ferric chlorides. As in the case of metallic silver, heat and the presence of salt promotes the reactions.

Experiments made by M. Vaygouny [1] show the action of ferric chloride on ores containing gold and silver as the sulphide. Vaygouny treated Tonapah ore with a solution made up of 1 to 2 per cent. ferric chloride, 15 to 20 per cent. common salt, and a little free hydrochloric acid, and charged with free chlorine. The Tonapah ore treated contained galena,

[1] *E. and M. J.*, Dec. 29, 1904.

pyrite, calcite, silver sulphide and gold, in a gangue consisting mainly of quartz. The ore was crushed to 80 mesh, warmed and kept boiling for 3 hours, care being taken that it was always well chlorinated. The results were as follows:

EXPERIMENT NO. 1. ORE NO. 1

Sample	Au oz. per ton	Ag oz. per ton
Original,	0.8	84.7
Tailings,	0.35	4.8

This corresponds to about 56 per cent. extraction of gold and 94.4 per cent. of the silver. In a similar experiment, crushing the ore to 120 mesh instead of to 80, the results were as follows:

EXPERIMENT NO. 2.

Sample	Au oz. per ton	Ag oz. per ton
Original,	1.03	86.2
Tailings,	0.125	1.1

This corresponds to about 88 per cent. extraction of gold, and 98.7 extraction of silver.

A similar experiment was carried out with the ore crushed to 120 mesh, but instead of treating it hot, the ore was treated 3 days cold. The results of this test were:

Sample	Au oz. per ton	Ag oz. per ton
Original,	1.03	86.2
Tailings,	0.325	6.6

This corresponds to 69 per cent. extraction of gold and 92.4 per cent. extraction of silver.

The reaction involved in converting the silver sulphide to the chloride by means of ferric chloride may be expressed as thus:

$$Ag_2S + 2FeCl_3 = 2AgCl + 2FeCl_2 + S.$$

To what extent the ferric chloride can be kept in solution in the presence of free chlorine is a question. In elaborate experiments made by John E. Greenawalt, at Denver, during the year 1900, with a view of chlorinating silver ores with chloride solutions, it was found that ferric chloride was decomposed, and ferric oxide was thrown out, forming quite a perceptible layer on top of the ore in the vats.

Chlorine, as is well known, very often acts as an oxidizing agent. It is probable that the ferric chloride is oxidized, in the presence of chlorine and water, to ferric oxide and hydrochloric formed at the same time.

Chlorine acts on silver to convert it into the chloride. It also acts on the sulphide in aqueous solution to convert the silver into the chloride and the sulphur of the sulphide is oxidized into sulphuric acid. Hydrochloric acid acts on silver slowly, to convert it into the chloride, hydrogen being evolved. The reaction takes place more rapidly when it is subjected to the combined action of hydrochloric acid and atmospheric air. Dilute hydrochloric acid has no action on silver sulphide.

Silver dissolves slightly at ordinary temperatures in an aqueous solution of ferric sulphate, and more readily and in greater proportions when free sulphuric acid is present. Chloride of silver is formed when hydrochloric acid or sodium chloride is added to a solution of sulphate of silver in water, or in water acidulated with sulphuric acid.

Silver chloride, may therefore, be formed either by chloridizing roasting, or by chlorine or some of the base metal chlorides. It is quite insoluble in water or in sulphate solutions. It is somewhat soluble in chloride solutions.

If sulphide copper ores contain considerable silver, and salt is cheaply available, it is best to give the ores a chloridizing roast. If the roasting is carefully done a very high percentage of both the copper and silver may be extracted with one solvent, and a fair percentage of the gold. In such cases an acid solution of salt would be used as the solvent for the copper and silver, and this solution could then be charged with free chlorine for the close extraction of the gold.

Hahn determined the solubility of silver chloride in solutions of different chlorides, as follows:[1]

Salt	Salt per cent.	Degree C. saturated at	AgCl per cent.	Ag per cent.	Degree C. temperature	Grams Ag in 100 c.c.
KCl.....	24.95	19.6	0.0776	0.0584	19.6	0.0688
NaCl.....	25.96	19.6	0.1053	0.0793	19.6	0.0956
NH_4Cl.....	28.45	24.5	0.3397	0.2551	30.0	0.2764
$CaCl_2$.....	41.26	24.5	0.5713	0.4300	30.0	0.6283
$MgCl_2$.....	36.35	24.5	0.5313	0.3999	30.0	0.5339
$BaCl_2$.....	27.32	24.5	0.570	0.0429	30.0	0.0558
$FeCl_2$.....	30.70	24.5	0.1686	0.1269	20.0	0.1802
$FeCl_3$.....	37.48	24.5	0.0058	0.0044	21.4	0.0064
$MnCl_2$.....	43.85	24.5	0.1996	0.1499	30.0	0.2226
$ZnCl_2$.....	53.34	24.5	0.0134	0.0101	30.0	0.0162
$CuCl_2$.....	44.48	24.5	0.0532	0.0399	30.0	0.0627
$PbCl_2$.....	0.99	24.5	0.0000	0.0000	30.0	0.0000

The salts most likely to be present, in leaching with a chloride solution, are cupric chloride, $CuCl_2$; sodium chloride, NaCl; and ferrous

[1] T. A. I. M. E., 1870.

chloride, $FeCl_2$, and these salts will hold in solution, 13.5 oz., 25.0 oz. and 40.5 oz. of silver, as chloride, per ton respectively, under conditions of maximum or almost maximum solubility. These conditions are never met with in practice, but the solubility of silver chloride in chloride solutions, as met with in practice, is quite sufficient to extract the silver under all conditions likely to occur in treating copper ores. Temperature is an important factor in dissolving silver chloride in solutions of other metal chlorides.

If there is silver in copper ore, the silver may be extracted simultaneously with the copper by using a chloride solution, and without any very special effort. As gold is not soluble in water nor in a chloride solution, it will be necessary to charge the chloride solution with chlorine before the gold can be extracted. If a sulphate solution is used, an ordinary solution of chlorine in water may be used to extract the gold, and if the ore contains silver and the copper is leached with sulphuric acid, the chlorine may be used in connection with a chloride solution, as is frequently done in extracting the precious metals by the Plattner process. The method of applying the chlorine to ores which have been given a preliminary treatment for copper, presents something of a problem.

The Plattner process, of gassing the ore, is not applicable, since the ore, once saturated and disintegrated with an acid solution to extract the copper, is not satisfactorily permeable with chlorine gas. To take the ore out of the vat and partially dry it to give it the proper moisture required for satisfactory gassing is too expensive.

Barrel chlorination is also too cumbersome. If the copper is extracted in the barrel, it follows that the barrel must again be separately charged with chemicals to extract the gold. If the ore contains silver also, further complications are introduced, since silver chloride is not soluble in water, and the use of chloride solutions in lead lined barrels is not advisable.

The most expedient way of using chlorine in connection with copper ores, is to use it in solution, and the cheapest way of producing it is by electrolysis, from common salt.

Chlorine is not readily soluble in water, and less soluble in a chloride solution; nor is the solubility as great in heated as in cold solutions. However, after the ore has been given an acid treatment for the extraction of copper, the consumption of chlorine is not as great as in the regular treatment of gold ores. Usually there will be no difficulty in getting sufficient chlorine in solution to treat the ordinary copper ores for gold. The chlorine solution, once obtained, is applied to the ore in ordinary leaching vats, if the copper has been extracted by percolation, or it may be applied in agitators if the copper has been extracted in agitators. The solubility of chlorine in water according to Schonfeld is as follows:

SOLUBILITY OF CHLORINE IN WATER

Temperature, degrees		Vols. Cl	Temperature, degrees		Vols. Cl
C.	F.		C.	F.	
10	50	2.58	30	86	1.75
15	59	2.37	35	95	1.55
20	68	2.16	40	104	1.36
25	77	1.95			

At 100° C., or 212° F., the solubility is zero.

A cubic foot of chlorine gas weighs approximately 3 oz. A cubic foot of water can hold 6 oz. of chlorine. One liter of chlorine gas weighs 3.17344 grm., under ordinary pressure, and is 2.45 times as heavy as air.

In making extensive tests, on a large scale in Denver, during the years 1900–1905 there was no difficulty in getting from 0.5 to 0.75 per cent. chlorine in a chloride solution; this corresponds to 10 to 15 lb. of chlorine per ton of solution. The solubility of the chlorine may be made greater and obtained quicker by absorbing it under pressure[1] when, according to Henry's law, the volume of chlorine absorbed will be directly proportional to the pressure of the gas. In this way a strong solution of chlorine may be quickly obtained with suitable apparatus.

The usual way of absorbing chlorine in water, is by passing the chlorine from the cells into the bottom of a scrubbing tower while the water showers down from above. It is not easy to get a strong solution of chlorine. The purity and the concentration of the gas has much to do with it. Some type of cells are likely to dilute the gas excessively with air; if the dilution is too great a weak solution of chlorine will result, and a weak solution is not as effective in treating ores as a strong solution. In using diaphragm cells it requires quite a delicate balance in operation to get a gas reasonably free from dilution with air, under the necessary suction to keep the cell room free from objectionable fumes.

ELECTROLYTIC CHLORINE

The cheapest way of producing chlorine is by the electrolysis of chlorides. Usually common salt is used for the purpose. Various electrolyzers have been invented to decompose salt into chlorine and caustic soda; these may be classified as follows: Mercury, diaphragm, gravity, and fusion cells. All these types have been, and most are now, in successful operation on enormously large scale for the manufacture of chlorine and caustic soda. Carbon is generally employed as the anode and iron as the cathode. Chlorine appears at the anode, while the sodium, re-

[1] U. S. Patent, 901, 611, Oct. 20, 1808, W. E. Greenawalt.

leased at the cathode, combines with water, to form caustic soda, hydrogen being released at the same time.

$$NaCl + \text{electric current} = Na + Cl.$$
$$Na + H_2O = NaOH + H.$$

Theoretical Data.—One ampere-hour will produce, by electrolysis of common salt, 1.3219 grm. of chlorine.

It takes 0.7565 ampere-hours to produce 1 grm. of chlorine. One ampere-hour will produce .002914 lb. of chlorine. It takes 343.1 ampere-hours to produce 1 lb. of chlorine. A current of 746 amperes per hour will release 2.173 lb. of chlorine per hour, which, when divided by the voltage at which the decomposition takes place, will give the pounds per horse-power-hour. A current of 1000 amperes per hour will release 2.9144 lb. of chlorine per hour, which, when divided by the voltage, will give the pounds per kilowatt-hour. 2.3 is the theoretical voltage for the decomposition of salt from aqueous solution.

Practical Data.—The following figures are given by Castner as the results of extended practical working of the Castner mercury cell (Fig. 64) for the production of chlorine and caustic soda. This cell was the first to achieve pronounced commercial success, and has been in operation at Niagara Falls and various parts of Europe for many years. A cell in operation, running at an efficiency of 88 per cent., gives the following actual results:

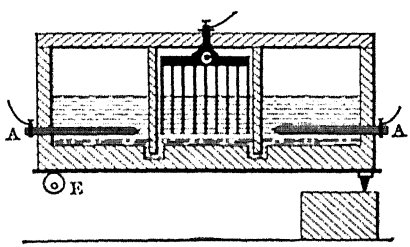


FIG. 64.—Castner chlorine cell.

The electromotive force required for each cell is 4 volts for a current of 550 amperes. Each cell, which is 6 ft. long, 3 ft. wide, and 6 in. deep, decomposes 56 1/2 lb. of salt daily, producing 38 1/2 lb. of caustic, and 34 1/2 lb. of chlorine, in 24 hours, for the expenditure of 3 1/2 indicated horse-power.

A cell (550 amperes) per hour, decomposes 1058 grm. of salt.
A cell (550 amperes) per hour, produces 724 grm. of caustic.
A cell (550 amperes) per hour, produces 642 grm. of chlorine.
A cell (550 amperes) per day, decomposes 56 1/2 salt.
A cell (550 amperes) per day, produces 38 1/2 lb. caustic.
A cell (550 amperes) per day, produces 34 1/2 lb. chlorine.
Actual electrical horse-power per cell, 3 h. p.
Indicated horse-power per cell, 3 1/2 h. p.
Salt decomposed per ampere-hour, 1.92 grm.
Salt decomposed per watt, 0.48 grm.
Salt decomposed per kilowatt, 1.06 grm.
Salt decomposed per indicated horse-power-hour, 295 grm.
Caustic produced per indicated horse-power-hour, 209 grm.
Chlorine produced per indicated horse-power-hour, 183 grm.

Salt decomposed per indicated horse-power-day, 16 lb.
Caustic produced per indicated horse-power-day, 11 lb.
Chlorine produced per indicated horse-power-day, 9.8 lb.

The chlorine gas from these cells is from 95 to 97 per cent. purity. The current efficiency of the Castner cell is about 88 to 90 per cent., and the energy efficiency about 52.3 per cent.

Fig. 64 shows a longitudinal section through the Castner cell. The apparatus is divided into three compartments, the two outside ones containing brine and the carbon anodes, while the middle one contains the caustic solution and the iron cathode. The sodium set free is taken up by the mercury, forming an amalgam. The cell is made to rock slightly

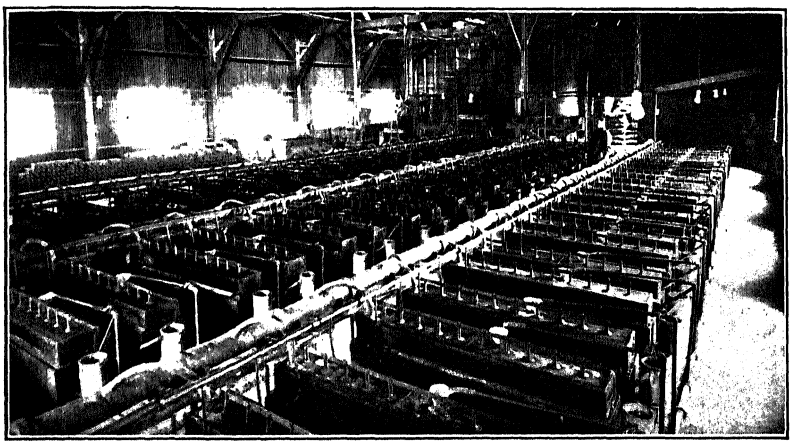


FIG. 65.—Electrolytic chlorine plant at the works of the U. S. Reduction and Refining Co., Colorado Springs, Colorado.

by a cam and the motion carries the mercury and amalgam into the center compartment, where the amalgam acts as the anode during the passage of the current to the cathode, the sodium being liberated. A regulated supply of water flows into the center compartment continuously, while a corresponding amount of caustic solution overflows into a collecting tank. The covers of the anode compartment have pipes for leading off the chlorine, but the cathode compartment is only loosely covered, so that the hydrogen escapes in the air.

The various types of cells give about the same practical results. The diaphragm cell is quite extensively used. In 1902 the author installed an experimental plant at the works of the Portland Gold Mining Co., at Colorado Springs, consisting of three diaphragm cells, using a current of 1000 amperes each, and arranged to treat the ore in one of the barrels, or on a basis of 30 tons per day. The results were highly encouraging, but the work was suspended. This was the first attempt to treat Cripple

Creek ores with electrolytically generated chlorine. At the present time, at the works of the U. S. Smelting & Refining Co., at Colorado Springs, from 300 to 400 tons of Cripple Creek ore are treated daily, in barrels, with chlorine generated electrolytically in 75 McDonald diaphragm cells (Fig. 65), producing 1500 lb. of chlorine in 24 hours. The McDonald cell, Fig. 66 consists of a cast-iron tank 1 ft. deep, 1 ft. wide and 5 ft. 2 in. long, with two longitudinal perforated partitions, thus dividing it into three compartments. The perforations are 1/32 in. in diameter, and there are four or five to the square inch.

Against each perforated side wall of the central or anode compartment of the tank is stretched a diaphragm, consisting of a layer of asbestos paper fastened to asbestos cloth by a small quantity of sodium silicate. This diaphragm is held in position by cement placed over the

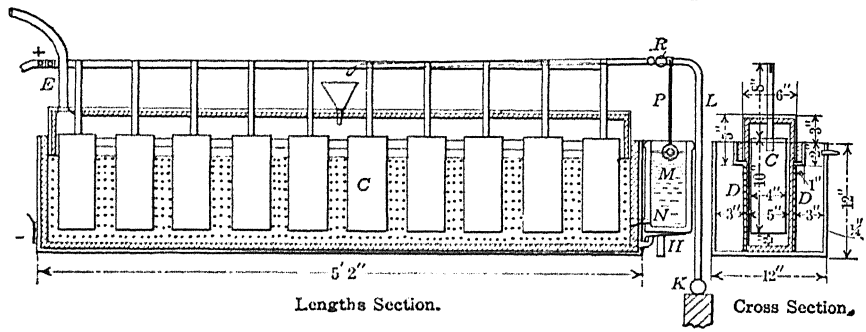


FIG. 66.—McDonald chlorine cells.

end walls and the bottom of the anode compartment. This compartment is closed by a cast-iron cover 5 in. deep, 6 in. wide, and nearly 5 ft. long, into which the anodes are cemented. It is lined with cement and painted with asbestos varnish.

The anodes consist of blocks of graphitized carbon, 4 in. square and 10 in. long, into which a copper rod is fastened by lead for the electrical connections. The partition walls form the cathode. The partition walls are flanged, forming a seat to hold the cover, which is surrounded by a layer of cement. The chlorine is conducted from the anode compartment, into absorption towers, and the chlorine solution is then applied to the ore. Brine circulates through the anode compartment. The sodium hydrate solution leaving the cathode compartment contains from 7 to 18 per cent. caustic soda. When the diaphragm is new, the level of the liquid in the anode and cathode compartments is nearly the same, but when it becomes more or less clogged, the depth of the liquid in the cathode compartment is only an inch or two. The diaphragms last about 8 months. Graphitized carbon leading-in rods, screwed into the anodes, will usually be found better than metal for the electrical connections in any cell.

Treatment of the Ore at the Mt. Morgan Mine.—The Mount Morgan mine,[1] in Australia, was formerly worked purely for the gold; as the pyritic ores were developed, copper in considerable quantities made its appearance so that now the metallurgical installation consists of a chlorination plant to treat the oxidized ores; a chlorination plant to treat the lower grade pyritic copper ores, and a smelting plant to treat the higher grade copper ores.

The oxidized ores are crushed in ball mills, and roasted, chiefly to effect dehydration and agglomeration. It is then charged into leaching vats, 16 in number, built of brick with cement mortar. They measure 60 ft. long, 12 ft. 6 in. wide, and are 6 ft. deep. The capacity of the vats is 200 tons. The leached ore is discharged by sluicing through side doors.

After the ore is charged into the vats, it is leveled off, and a water wash is given to cool the ore. When the wash water has drained, a solution of chlorine water is run on and kept slowly leaching until the effluent liquor smells strongly of chlorine. The vat is then placed "in contact" for 8 hours. After the solution has leached off another chlorine wash is given, followed by a water wash. The actual time consumed is: (1) Water wash to cool ore, 24 hours; (2) chlorine solution, 30 hours; (3) washing out with water, 18 hours. When the water wash no longer carries gold the contents of the vat are sluiced down the creek. The consumption of chlorine averages 2.5 lb. per ton of ore. The gold-bearing solutions are pumped to storage vats from which they are delivered to 12 charcoal filters of brick-lined concrete, $10 \times 12 \times 5$ ft., each holding 2 tons of charcoal. The precipitation is absolute and the effluent liquors from the boxes contain no free chlorine. At present the ore averages 4 dwt. and a recovery of 95 per cent. is effected. The costs for 117,000 tons treated for the year ending May 31, 1908, were: crushing, 87 cents; roasting, 93.5 cents; chlorination, 75 cents; total $2.56.

The ore treated at the mundic works has the following general composition; silica, 68 per cent., pyrite, 26 per cent.; copper, 1 per cent.; and magnesia and alumina, 5 per cent. The gold averages 10 dwt.

The ore breakers are placed at the main incline shaft and after breaking down to 1-in. cubes it is delivered to the mill bins by an electric tram. The bins have a capacity of 2000 tons, and the plant is designed to treat 11,000 tons per month. The plant is divided into two units, each of which comprises one tubular dryer, and an elevator for the delivery of the dried ore to the mill bins. The ore is fed to seven No. 5 Krupp mills. The crushed ore is then delivered to the roasting furnaces, where it occupies 24 hours in transit through the furnace. The consumption of wood fuel is equal to 18 per cent. of the weight of ore treated. From the finishing hearth of the furnace the ore is delivered by conveyors to the vats. There are eight vats of 200 tons capacity, two of 400 tons and two of 1000 tons capacity. The vats are constructed of brick, set in cement

[1] Gerald Williams, *E. and M. J.*, April 17, 1909.

and are provided with sluice gates at the sides for the discharge of the leached ore. The course of treatment is as follows;

1. Acid wash of 0.2 per cent. sulphuric acid followed by a water wash. This removes about 50 per cent. of the copper which is precipitated in tanks filled with scrap iron. The acid treatment and water wash occuping about 2 days.

2. Three days' treatment with chlorine solution.

3. Water wash, from 1 day in the smaller vats to 3 days in the 1000-ton vats. The residues are sluiced down into a dam where they accumulate. The spent liquors from the precipitation works are pumped to the dam and the leachings are precipitated with scrap iron. The residues contain 0.4 per cent. copper which is slowly recovered from the leachings.

The recovery of the gold on 10 dwt. ore is 96 per cent. The charcoal from the precipitation boxes in both the west and mundic works is treated at a central refinery. After burning off in large muffles the ash is smelted in a reverberatory furnace with sand and soda, and the bullion is tapped into moulds. From the moulds the bullion is remelted in large graphite crucibles in circular coke-fired furnaces. The bullion is refined with air which is blown through the molten metal. The cost of treating 115,000 tons of ore during the year ending May, 1908, was: crushing, 78.8 cents; roasting, $1.367; chlorination, $1.01; total, $3.174.

The chlorine used in the solution of the gold was formerly generated in stills made of slabs of sandstone, from a charge of manganese ore, salt, and sulphuric acid, the mixture being heated and kept mixed by jets of steam entering at the bottom of the sides. The chlorine gas is led in earthenware pipes to the bottom of concrete scrubbing towers where the gas rises against a falling stream of water and is absorbed by it. The strength of solution is generally 80 gr. per gallon.[1] Recently a plant has been installed to generate the chlorine direct from common salt, by electrolysis.

A comparison of the smelting operation with the hydrometallurgical process, is interesting. The ore sent to the smelter[2] has the following composition: silica, 45 per cent.; iron, 25; sulphur, 25; copper 3.5; alumina 1.5 per cent. Iron ore is obtained from the company's mine at Iron island, a small island at the mouth of Kepple bay, 18 hours' steam from Rockhampton. The company pays a small royalty and mines the ore with its own men. Two steamers are engaged in bringing ore from the island to the wharves at Rockhampton. The limestone is obtained from the companies' (*i. e.*, Geromes, owned by the Mt. Morgan Company) quarries at Marmor, 35 miles by rail from Mount Morgan.

The limestone contains only 2 per cent. silica. Delivered into the

[1] Bowie Wilson, *E. and M. J.*, April 24, 1909.
[2] Gerard Williams, *E. and M. J.*, April 17, 1909.

smelter bins iron ore costs $4.44, limestone, $1.60 and coke $9.50 per ton. The normal daily charge for each furnace is as follows: Ore, 200 tons; limestone, 100 tons; iron ore, 45 tons; low grade mattes (purchased) and converter slags, 15 tons; coke, 40 tons. The resulting matte is converted into blister copper averaging 99.1 per cent. Cu, and 12 oz. gold, and then refined electrolytically.

Treatment of the Auriferous Copper Ores at Falun, Sweden.[1] The ore is roasted at a low temperature with a view of obtaining the copper in the form of sulphate. If silver is present salt is added in the roasting furnace. The roasted ore is then placed in false-bottomed, wooden vats and leached with hot water, followed, if necessary, by hot dilute sulphuric or hydrochloric acids, by which all the copper and much of the iron are removed from the ore. The solutions thus obtained are run through tanks containing scrap iron, by which the copper and silver in solution are precipitated. The solution of ferrous sulphate may be saved and used subsequently to precipitate the gold. The residues in the vats are now in a condition to yield up their gold readily, and are accordingly treated with a solution of 0.6 to 0.7 per cent of chloride of lime (bleaching powder) in water, mixed with an equal volume of dilute hydrochloric acid of specific gravity 1.002 or 1.003, or of dilute sulphuric acid. These solutions were mixed in troughs just before they flowed into the ore vats. The liquid passes though the ore until the gold ceases to be dissolved, after which the tailings are thrown away. The solution is heated to 160° F. by steam, and precipitated with ferrous sulphate. The collection of the gold is expedited and ensured by adding acetate of lead to the solution; by this device lead sulphate is precipitated with the gold, and in settling to the bottom, carries the particles of precious metals with it. This process was in continuous operation at the Falun works from 1885 to 1888. In that period, 1500 tons of gold ore and the tailings from 29,000 tons of copper ore were subjected to treatment. It is stated that in the year 1886, the tailings from 14,000 tons of copper ore were treated with the following results:

AVERAGE AMOUNT OF GOLD IN TAILINGS

Before treatment, 41.82 grains per ton.
After treatmnt, 4.04 grains per ton.

COST PER TON

Chloride of lime (6 lb.),	5 d.
Sulphuric acid (8.37 lb.)	1 d.
Lead acetate and other reagents,	3/4d.
Fuel for steam,	1 1/4d.
Labor,	1 d.
Total,	9 d. = 17.25¢.

[1] Rose, "The Metallurgy of Gold," p. 268.

CHAPTER XIV

TREATMENT OF ZINCIFEROUS COPPER ORES

Zinciferous copper deposits are quite common in the western United States, Mexico, and other parts of the world. In many of these deposits the zinc and copper sulphide minerals are so intimately associated as to defy all attempts at mechanical separation. No serious attempt has yet been made to treat these ores chemically.

Theoretically the chemical separation of the copper and zinc from such ores would not appear difficult, since both copper and zinc, after roasting, are readily soluble in dilute acid solutions. The copper may be readily precipitated from the solution either by chemical reagents or by electrolysis, while the zinc remains unaffected. After the copper is precipitated, the zinc may be recovered free from copper and other impurities, either by electrolysis at a higher voltage, or by evaporation as the sulphate or chloride of zinc, for which there is a limited sale. The extraction of the zinc and copper from the ore presents no serious difficulty, but the recovery of the dissolved zinc from the solution, is an exceedingly difficult problem, and unless some method can be devised for recovering the zinc at a profit, it is evident that the consumption of acid is such that the copper cannot be recovered at a profit, and hence the deposits remain unworkable under the present conditions.

If a zinciferous copper sulphide ore is roasted, and then treated with sulphuric or hydrochloric acid, the copper and zinc will go into solution as sulphates or chlorides. The copper may then be precipitated from the solution by any of the well-known methods, and the precipitated solution returned to the ore, as in a cyclic process, until the solution becomes saturated with zinc sulphate or chloride. The solution can then be purified, usually by displacing the impurities by zinc and zinc oxide, while a corresponding amount of zinc goes into solution. The solution, now purified and saturated with zinc sulphate or zinc chloride, may be evaporated to get the crystallized salts, if a market is available, or better, it may be treated, electrolytically to extract the zinc in the metallic condition; but in the electrolysis of the zinc salts is the crux of the entire problem.

The commercial electrolysis of zinc solutions, either acid or alkaline, has not yet been accomplished, although as the cause of the difficulties are becoming better understood, the problem may sooner or later be satisfactorily solved. The problem is further complicated by the fact that it takes about 4 times as much power to deposit a pound of zinc as

a pound of copper, and the price of the metallic zinc is only about half that of copper. On the other hand, the zinc may be regarded as a by-product, for which nothing is paid in the crude form, and the smelters usually penalize the zinc in copper ore, when above 5 to 10 per cent.

With solutions of zinc salts, both acid and alkaline, and especially if the solution is dilute and the current density small, powdery, spongy deposits of zinc, which appear often almost black in color while wet, are obtained on the cathode. If the solution is excessively acid, no deposit will result, as the zinc is dissolved as rapidly as deposited, and the solution need not be highly acid to seriously affect the amount of zinc deposited. The zinc sponge is not as likely to occur from an acid as from an alkaline or neutral solution. Zinc deposited in a spongy form cannot be melted down on account of its tendency to oxidize.

It is a peculiarity of this zinc sponge that solutions which will perhaps for half an hour yield quite satisfactory reguline deposits of zinc will, when a certain thickness has been attained, commence to deposit the spongy metal, and this may occur in neutral, acid, or alkaline solutions. Two theories have been advanced as to the cause of this unsatisfactory deposit, namely, one that it is due to the formation of a hydride of zinc and is due to the liberation of free hydrogen with the zinc at the cathode, and the other that it is due to the formation of zinc hydrate.

The formation of spongy zinc, may apparently be avoided by using strong solutions with only small amounts of acid present and using high current densities, of from 15 to 30 amperes per square foot, and by employing rapid circulation of the electrolyte. The formation of zinc sponge from solutions which to commence with yield good reguline deposits, is probably due to the impoverishment in zinc salt of the electrolyte in contact with the cathode.

The electromotive force required for the decomposition of zinc sulphate is 2.35 volts, and for zinc chloride 2.43 volts. 1.2194 grm. are deposited from zinc solutions by 1 ampere-hour, 2.6883 lb. per 1000 ampere-hours. In practice the electromotive force required will not usually be less than from 3 to 3.5 volts.

Iron generally occurs in the neutral or feebly basic solutions as ferrous salt. It can only be precipitated out of the solution after the conversion into a ferric salt. Iron can be removed from sulphate solutions of zinc by the addition of carbonate of lime, and passing a current of air through the solution. If the iron is present as chloride and not in too large quantity, it is best oxidized and precipitated by the addition of a small quantity of chloride of lime; the calcium chloride so formed has no injurious effect on the electrolysis. Any electronegative metals that may be present in the solution may be precipitated with zinc dust.

In the electrolysis of sulphate solutions with lead anodes, the anodes gradually become covered with a superficial layer of peroxide of lead, and

must be freed from it by being washed from time to time. As soon as the electrolyte contains 9 to 9 1/2 oz. of sulphuric acid per gallon, a current density of 10 amperes per square foot can no longer deposit zinc from it. Before, therefore, the free acid present reaches this amount, the electrolyte must be replaced by a solution of neutral sulphate.

In the Cowper-Coles process, the finely ground ore containing the zinc is converted into the oxide and sulphate by roasting, and then leached with a dilute acid solution of zinc sulphate. The leaching is done in vessels fitted with filters, and is facilitated by the passage of an electric current through the acid liquid, insoluble anodes and zinc cathodes being employed. The copper goes into solution with the zinc, and is precipitated in tanks, the bottoms of which are covered with a layer of charcoal and iron or zinc. When the solution contains 15 to 20 per cent. of zinc sulphate, it is electrolyzed between lead anodes and rotating cathodes in the form of discs of sheet iron.

Neutral concentrated solutions of zinc sulphate dissolve small quantities of zinc oxide, so that these solutions give compact zinc during the first hour of electrolysis. The liquid, however, soon becomes basic, due to the oxidation of zinc, and the sponge is then deposited. To prevent this it is necessary to maintain the solution slightly acid; continuous agitation of the electrolyte is also necessary otherwise it becomes too dilute at the cathode.

Hoepfner considers that an active motion of the electrolyte by means of rotating cathodes is necessary for the production of dense deposits. In this way hydrogen bubbles, which have clung to the cathodes are removed, and the formation of ragged edges by the abnormally high and uneven current densities is prevented.

One of the inherent difficulties in the electrolysis of zinc compounds is that the heat of combination is generally rather high, thus necessitating the expenditure of a relatively high power; and for the same reason other metals are apt to be deposited first, thus necessitating a pure solution. Hoepfner was one of the first to realize these difficulties, and was one of the first, if not the first, to devise a process which was for some time in operation on a commercial scale.

The Hoepfner Zinc Process was in use in Fuhrfort, Germany, from 1895 to 1897, but was discontinued, although it was claimed, this was for personal and not for technical reasons. It is now in operation in Hrusshau, Austria, and at the works of Brunner, Mond, and Company, at Winnington, England. Guenther[1] gives a long illustrated description of this process, which is briefly as follows: The raw material was the cinder from zinciferous pyrite, mined in Westphalia, the zinc tenor of this cinder varying from 10 to 16 per cent. The prepar-

[1] *E. and M. J.*, May 16, 1903.

atory treatment consisted in grinding the cinder to 1.5 mm. size, mixing with 18 to 20 per cent. common salt, and roasting in a muffle furnace for 20 to 24 hours at a temperature of not over 650° C. The charge of the cinder per furnace was 4500 kg. and the coal consumption 900 kg. per charge. The charge drawn from the furnace was leached, while still hot, in iron vats with water or dilute liquor from a subsequent stage of the process, affording a solution containing about 10 per cent. zinc, besides sodium chloride, sodium sulphate, and small quantities of lead, copper, cadmium, arsenic, manganese and thallium. The sodium sulphate was crystallized out as $Na_2SO_4+16H_2O$ by cooling the solution to $-5°$ C., after which the iron and manganese were precipitated by the addition of bleaching powder and marble dust, and finally the electronegative metals by means of zinc dust. A clear solution of the chlorides of zinc and sodium was thus obtained, which on the average assayed 20 per cent. $ZnCl_2$, 22 per cent. NaCl, 0.05 per cent. to 0.06 per cent. H_2SO_4, and traces of lead, iron, and thallium, and after acidification with a small amount of hydrochloric acid, free from arsenic, was ready for electrolysis. The electrode vats were V-shaped tubs; the anode and cathode compartments were separated from each other by means of a diaphragm of nitrated cloth. Artificial carbons, hard as glass, were used as anodes, while the cathodes consisted of discs of zinc or iron, arranged vertically on a horizontal shaft so as to revolve between a pair of adjacent anode cells.

The electrolyte entered each vat on one of the horizontal sides and came out at the top of the opposite side, so there was only a circulation past the cathodes, but the solution could pass beneath the anode cells. The diaphragms which were closed on top, where they were made air tight by means of melted pitch, prevented a rapid motion in the anode cells. The solution entering the vat had a tenor of 9.5 to 10 per cent. Zn, and the tenor of zinc in both should not be less than 2 per cent. The acidity to be maintained at 0.08 to 0.12 per cent. HCl, and during the electrolysis acid was added to the extent of 0.03 to 0.05 grm. HCl per ampere-hour. A good deposit of zinc could not be obtained from neutral or alkaline solutions. The vats were connected in series and a current density of 100 amperes per square meter used, which, it was thought, was less than desirable; the terminal voltage of the bath was 3.3 to 3.6 volts. In regular operation zinc deposited on the cathodes in dense form, silver white in color, and the current efficiency was 97 per cent. or more, of the theoretical. After 30 to 35 days, when 800 to 1000 kg. of zinc had been deposited, the cathodes were replaced by a new set. The zinc was then remelted in a reverberatory furnace, losing 1.5 to 2 per cent. in weight, wherein the consumption of coal was 7 to 8 per cent., the final product assayed 99.97 to 99.98 per cent. Zn, 0.01 to 0.02 per cent. Pb, and traces or iron and thallium. The anode cells had an outlet pipe of glass or hard

rubber; the chlorine gas liberated by electrolysis was used for makir bleaching powder.

The electrolysis of fused zinc chloride has frequently been suggeste and tried, but up to the present time the most encouraging results ha been obtained with chloride solutions.

The electro deposition of zinc from alkaline solutions has also bee repeatedly proposed, but has not come into use.

CHAPTER XV

TREATMENT OF COPPER-NICKEL ORE AND MATTE

Nickel is frequently associated with copper ores, in quantities worth recovering. The ordinary method of recovering the nickel in such ores, as for example at Sudburry, is to smelt to a copper-nickel matte, and then recover the metallic copper and metallic nickel from the matte by further metallurgical treatment.

If a hydrometallurgical process is used to extract the copper from ores containing small quantities of nickel, the process is carried out the same as if no nickel were present, and when the nickel, as in a cyclic process, has accumulated sufficiently in the solution, it may be recovered therefrom by either chemical or electrolytic methods.

Nickel is only extracted with considerable difficulty direct from its ores, especially if in the form of silicate (Garnierite), and most nickel ores are not entirely free from this mineralogical combination.

The solutions which are used for recovering nickel from copper ores, mattes, or alloys, are either dilute sulphuric or dilute hydrochloric acid. The copper in either solution, preparatory to precipitating the nickel, is reduced below 1 per cent. by electrolysis and finally completely removed by precipitation with metallic iron, or else hydrogen sulphide may be used, the excess of which is afterwards expelled.

The purified solution is rendered alkaline, filtered to remove precipitates, and the nickel recovered by electrolysis in suitable electrolyzers, using lead anodes for sulphate solutions and graphite anodes for chloride solutions. Both nickel chloride and nickel sulphate are freely soluble in water. Nickel chloride, $NiCl_2 6H_2O$, is easily soluble in water; 100 c.c. saturated water solution at 20° C., contains 39 gr. $NiCl_2$; 100 c.c. saturated water solution at 40° C. contains 42 gr. $NiCl_2$. Nickel sulphate; $NiSO_4 \cdot 7H_2O$, soluble in three parts of water at 20° C.; soluble in two parts of water at 50° C.

It is quite difficult to get a good coherent electrolytic deposit of nickel of any reasonable thickness. There is a difference of opinion as to the cause of solid, adherent deposits of nickel; some metallurgists claim that the most satisfactory deposits are obtained from alkaline electrolytes, whereas others say that the electrolyte must be acid. The general opinion, however, is that the non-adherent deposits are due to; the

electrolyte being too acid, the temperature of the electrolyte being too low, or else the cathode is not clean. Pulverent deposits are due to: too high a current density, too high an e. m. f., and too acid electrolyte.

The formation of insoluble salts is prevented by acidifying the electrolyte with weak acid, such as boric, perchloric, perbromic, or an organic acid, or else with a slight amount of sulphuric or hydrochloric acid.

Conditions which favor solid adherent deposits of nickel are: slightly acid electrolyte, to prevent basic salts; pure electrolyte; gas free electrolyte; temperature between 40 and 65° C.; constant current density; low e. m. f.; efficient circulation; clean cathode, and concentrated electrolyte.

Concentrated electrolytes, especially those consisting of very soluble nickel salts, give the most satisfactory deposits, other conditions being equal.

The tendency of nickel deposits to curl is greatest with high current densities, said to be due to the formation of nickel hydride, which is the result of greater liberation of hydrogen with high current density and high e. m. f.

Dr. Edward F. Kern and Francis G. Fabian[1] by exhaustive experiments, with cast-nickel anodes conaining 92 per cent. nickel, 5 per cent. iron, carbon and a trace of copper and using sheet-nickel cathodes placed 1 in. from the anodes, came to the following conclusions:

The presence of free acid in nickel chloride, nickel sulphate, and nickel fluosilicate electrolytes caused a very low cathode efficiency, whereas the anode efficiency was in most cases over 95 per cent. By continued electrolysis the free acid was neutralized and the cathode efficiency increased.

The electrolysis of neutral chloride and fluosilicate solutions with current densities of 10 to 20 amperes per square foot, gave very satisfactory deposits, and high current efficiencies. Neutral sulphate solutions were unsatisfactory, as precipitates of insoluble basic salts formed and intermixed with the deposited nickel.

Heating the chloride electrolyte decreased the e. m. f., increased the current efficiency and improved the deposition. The most satisfactory temperature was about 50° C.

A small amount of basic salts separated during electrolysis from the neutral chloride electrolytes, but did not interfere with the deposition. The presence of a small amount of free acid prevented their formation.

The results obtained by Kern and Fabian for nickel chloride and nickel sulphate electrolytes are summarized by the following table:

[1] *School of Mines Quarterly*, July, 1908.

Composition of the electrolytes	Temperature deg. C.	C. D. amperes per sq. ft.	Time of run minutes	$NiCl_2$ electrolyte		$NiSO_4$ electrolyte	
				Average e. m. f. in volts	Cathode current efficiency	Average e. m. f. in volts	Cathode current efficiency
Eight per cent. nickel and half molecular equivalent of free acid.	20	10	180	0.49	3.20%	0.89	0.86%
	40	10	180	0.36	1.25%	0.65	0.78%
	60	10	180	0.21	1.01%	0.42	0.39%
Eight per cent. nickel and 1/10 the molecular equivalent of free acid.	20	10	255	0.73	62.6%	0.91	1.50%
	40	10	255	0.52	79.0%	0.78	1.60%
	60	10	255	0.35	71.0%	0.51	1.50%
Eight per cent. nickel and 1/20 to 1/25 the molecular equivalent of free acid.	20	12	180	0.86	67.2%	0.97	0.00%
	40	12	180	0.53	75.7%	0.79	0.7%
	60	12	180	0.44	80.7%	0.61	2.8%
Neutral solutions containing 8 per cent. nickel.	20	10	255	0.78	96.6%	1.50	102.2%
	40	10	255	0.59	99.4%	1.35	106.9%
	60	10	255	0.44	99.2%	0.88	101.1%
Neutral solutions containing 8 per cent. nickel.	20	20	480	1.06	91.2%	3.45	
	40	20	480	0.73	94.7%	2.30	
	60	20	480	0.64	88.3%	1.40	
Neutral solutions containing 8 per cent. nickel and a half molecular equivalent of sodium salt.	20	20	180	1.02	90.1%	3.12	10.2%
	60	60	180	0.58	99.7%	0.96	99.8%

In the direct treatment of copper-nickel ore or matte, the copper and nickel are dissolved, usually with a chloride or sulphate solution. The copper may be precipitated chemically or electrolytically; the electrolytic method is preferred. In either case, the copper is precipitated in the ordinary operation of the process, while the nickel keeps accumulating in the solution, until its recovery therefrom becomes necessary or advisable. The copper in the solution, rich in nickel, is then completely removed, by chemical precipitation; after which the other impurities are removed, and the solution then electrolyzed to deposit the nickel.

When it is attempted to deposit nickel electrolytically, it is found that after a certain thickness is exceeded the metal detaches itself from the cathode and curls up in thin flakes. These are too thin to collect and melt to an ingot with economy and ease.

The observance of the conditions above stated tend to overcome the difficulty. Rapid rotation of the cathode also tends to permit of a thicker deposit.

The theoretical electromotive force required to decompose nickel and cobalt chlorides and sulphates is:

$NiCl_2$, 1.85 volts. $CoCl_2$, 1.78 volts.
$NiSo_4$, 2.09 volts. $CoSO_4$, 1.92 volts.

In the ordinary treatment of Copper-nickel ores, roasting and smelting, followed by converter treatment, yields a high-grade copper-nickel matte, and the problem is to separate the nickel from the copper. This is being done on a very large scale by the Oxford process, at the works of the Oxford Copper Co. The practice there is to smelt the matte containing sulphides of nickel, copper, and iron, in a cupola furnace, together with a charge of coke and sulphate of sodium, in the form of crude niter cake. The carbon of the coke reduces the sodium sulphate to sodium sulphide, and as this material when fused has a solvent action upon the copper and iron sulphides contained in the matte it will dissolve them to a considerable extent, so that when the molten contents of the furnace are tapped into settling pots the material will stratify. Sulphide of nickel, together with some sulphide of sodium, will settle to the bottom, and the sulphide of sodium, with copper and iron sulphides in solution, will float on top. The mass when solidified is divided into tops and bottoms, the tops containing sulphides of copper, iron, and sodium, and the bottoms containing sulphides of nickel, together with such of the sulphides of copper and iron as have not been taken up in solution in the sulphide of sodium. The bottoms are again charged into the smelting furnace with sodium sulphate, and are resmelted a sufficient number of times to purify the material to such an extent as to leave the nickel therein nearly free from copper, generally reducing the copper to less than 1 per cent. After having thus been treated the bottoms are crushed and leached for the purpose of removing the soluble portions of the sodium compound, and the product is dried and roasted, and is then mixed with sodium chloride and sodium sulphate and again roasted. The sodium chloride and sodium sulphate react to produce chlorine gas, which converts the copper contained in the mass partially to the form of copper chloride, and the remainder of the copper to copper sulphate, the nickel being converted largely to the form of nickel oxide and partially to the form of nickel sulphate. The residuum is then rewashed with dilute sulphuric acid, which removes the copper as sulphate, but does not attack the nickel oxide. It has been the practice to precipitate the metals from these solutions by the addition of sodium carbonate or sodium sulphide and then to remove the precipitate by passing the liquor through filter presses. The residues from the leaching consisting principally of nickel oxide, with a little silica, sulphur, copper, and iron, is then reduced in a crucible or blast furnace to crude nickel, which may then be refined electrolytically, if refined nickel is desired.

Recently much of the copper-nickel material is converted directly into Monel Metal, which is an alloy of copper and nickel, so that no separation of these metals is required for purposes for which Monel Metal is adapted.

To get pure nickel, electrolytic methods early suggested themselves

on account of the analogy with copper refining. For a number of years experiments were made to devise an electrolytic process. Until recently, most of these methods were unsuccessful. An unsuccessful experimental trial was made by Hoepfner at the works of the Canadian Copper Co. in which success was later attained on a somewhat similar process, by D. H. Browne, who was at that time chief chemist of the company. About the same time the Oxford Copper Co., while using the alkaline sulphide smelting process on a large scale, for a number of years, produced a certain amount of refined nickel at the Balbach Works in Newark, by the electrolytic process of their chief engineer, William Thum. Considerable experimental work was also done at the Bayone works of the Oxford Copper Co., by an electrolytic process devised by N. V. Hybinette. Still later, by Camillo C. Cito, which is in use at the Irvington Smelting & Refining Works, at Irvington, N. J.

The Hoepfner Nickel Process.—The Hoepfner process for the treatment of copper-nickel ore or matte, is not essentially different from his process of extracting copper alone. It may be described as follows:[1] The copper-nickel bearing material was ground to 60 mesh and then subjected to a leaching process with a solution of cupric chloride containing from 50 to 75 grm. of copper per liter. The leaching was done in revolving drums of about 5 cubic meters capacity.

The reactions taking place during leaching are:

$$(1)\quad CuS + CuCl_2 = Cu_2Cl_2 + S.$$
$$(2)\quad NiS + 2CuCl_2 = Cu_2Cl_2 + NiCl_2 + S.$$
$$(3)\quad Ag_2S + 2CuCl_2 = 2AgCl + Cu_2Cl_2 + S.$$

Iron also goes into solution,

$$(4)\quad FeS + 2CuCl_2 = Cu_2Cl_2 + FeCl_2 + S.$$

Lead, cobalt, zinc, etc., also go into solution if present in the raw material. The solution, after being thoroughly reduced by the copper-nickel matte or ore, was allowed to cool and clarify, and after removing the small amount of silver by precipitation with metallic copper, was subjected to electrolysis.

The electrolyte consists, after purification, of cuprous chloride, and nickel chloride dissolved in a sodium or calcium chloride solution. This electrolyte was conveyed to diaphragm cells in two separate channels, one going to the anodes and the other to the cathodes. The cathode solution, by electrolysis, was deprived of its copper, while the anode solution, through the action of liberated chlorine, was oxidized back to cupric chloride. The regenerated cupric chloride solution coming from the anodes was returned to the ore or matte and the cycle repeated.

[1] U. S. Pat. 704,640, July 15, 1902; *Electrochemical Industry*, Nov. 1903.

The cathode solution after being deprived of its copper contents, consisted of nickel chloride solution, which after thorough purification, was again electrolyzed at a higher voltage in cells having closed anode compartments and carbon electrodes. The cathodes consisted of revolving sheet-iron discs, upon which the nickel was deposited. The chlorine liberated during electrolysis was absorbed in a series of towers and vats by means of crushed matte and a solution of mixed chlorides. The towers were equipped with ejectors which kept the entire system under a partial vacuum, which prevented the escape or loss of chlorine. A jet of superheated steam was used in the agitation of the matte in a cupric chloride solution.

The reaction taking place during electrolysis may be summarized as follows:

$$(5)\quad Cu_2Cl_2 + 2NiCl_2 + \text{electric current} = 2Cu + 2NiCl_2 + Cl_2$$

the nickel chloride remaining unaffected during copper electrolysis, and the chlorine reacts with the cuprous chloride at the anode to form cupric chloride:

$$(6)\quad Cu_2Cl_2 + 2Cl = 2CuCl_2.$$

In the electrolysis of nickel chloride:

$$(7)\quad NiCl_2 + \text{current} = Ni + 2Cl.$$

The Browne Process.—The Browne process was in commerical operation for some years in Cleveland, Ohio, producing 1000 lb. of nickel daily, and a corresponding amount of copper, when in 1902 the plant was acquired by the nickel trust, and closed.

In the Browne process[1] the matte, crushed to about 1 mm. was first roasted to free it from sulphur. It was then reduced in a melting furnace by means of charcoal, and one half of the fused copper-nickel was cast into anodes and the othe half poured into water, thus giving copper-nickel shot of a weight equal to that of the anodes. The anodes were placed in the copper-nickel electrolyzers and the shot was placed in a tower. The composition of the copper-nickel anodes and shot was 54 per cent. copper, 34 per cent. nickel, the remainder being iron and sulphur; the iron usually ranging below 1 per cent.

In the Browne process, Fig. 67, *A* represents the tower in which the copper-nickel matte is placed for treatment; *B*, the Copper Electrolyzer; and *C* the nickel electrolyzer. The shot in the tower is subjected stimultaneously to the action of a stream of a solvent of cuprous chloride, such as salt water, introduced into the top of the tower, and a stream of free chlorine introduced at the side of the tower. The combined action of the salt water and the heat produced by the combination of the chlo-

[1] *Electrochemical Industry*, July 1903, U. S. Pat. 714,861, Dec. 2, 1902.

rine with the copper-nickel alloy form a solution of cuprous and nickel chlorides, the reaction being:

$$2CuNi + 6Cl = Cu_2Cl_2 + 2NiCl_2.$$

The solution so produced flows from the bottom of the tower into a reservoir tank from which it is drawn into the copper electrolyzers as desired, containing an anode of the copper-nickel metal and a cathode of

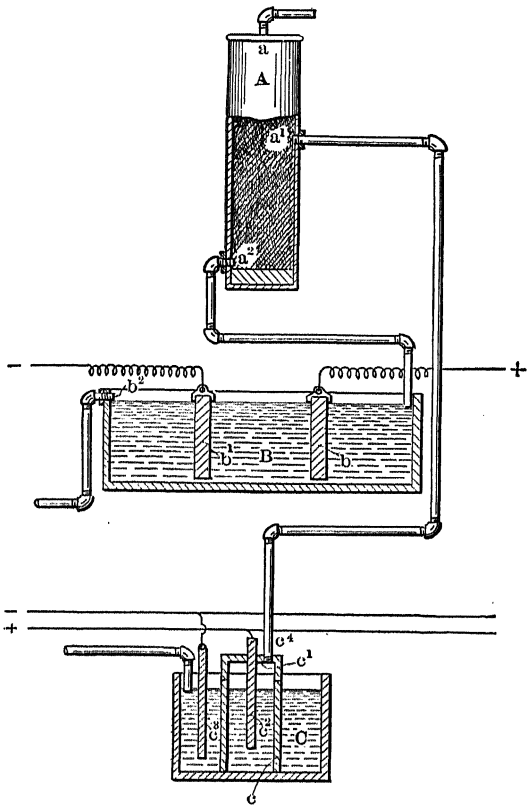


FIG. 67.—Browne process. Diagrammatic sketch.

sheet copper. The electric current passing through the solution of cuprous and nickel chlorides, the cuprous chloride is decomposed and the copper deposited upon the cathodes, while the chlorine combines with the copper and nickel of the anode, forming cuprous chloride and additional nickel chloride, the reaction being:

$$2CuNi + 6Cl = Cu_2Cl_2 + 2NiCl_2.$$

The cuprous chloride so formed is also decomposed in the same manner as was that of the original solution, cuprous and nickel chlorides being formed from the anode as before, copper plating out.

In the electrolyzers the ordinary multiple system was used. The anodes had a surface of 75×60 cm. and were 2.5 cm. thick. Concrete tanks were used; their dimensions were 256 cm. long, 85 cm. wide, and 67 cm. deep (about 9 ft. long, 3 ft wide, and 2 ft. deep.) Circulation was effected by overflow from cell to cell. The cathodes were thin electrolytically made sheets of copper. For 24 cells connected in series, the voltage varied from 6 to 10 volts, the current was 500 amperes. The copper was deposited in a coherent, although not dense form; it was sufficiently adherent, but was more crystalline than the copper of copper refineries. Between 2 and 2.25 grams of copper were produced per ampere-hour, while the theoretical value is 2.36 grm. A small amount of $CuCl_2$ in the electrolyte is sufficient to account for this difference from the theoretical value.

The proportion of nickel and copper in the fresh electrolyte applied to the cells was the same as in the anodes, as the electrolyte was made from the copper-nickel shot, which in its chemical composition was identical with the anodes. The electrolyte was a mixture of Cu_2Cl_2, $NiCl_2$, NaCl, and $FeCl_2$. After electrolysis in the copper cells, the proportion of nickel to copper in the issuing electrolyte was 80 to 1. The cathodes were recovered from the cells after three or four weeks. While the copper thus produced was not dense and of a very crystalline structure, a single melting process was sufficient to change it into commercial metal. The silver in the anodes passed completely over to the cathodes, but the copper-nickel alloy was very poor in silver. The anode scrap was returned to the furnace.

The electrolyte issuing from the cells and deprived of most of the copper, still contained about 1 part of copper to 80 parts of nickel; this remaining 1.25 per cent. of copper was chemically precipitated by treating the electrolyte issuing from the copper cells, with sodium sulphide and then filtering off the precipitated cuprous sulphide.

The solution then consisted of a mixture of $NiCl_2$, NaCl, and a small amount of $FeCl_2$. This solution was then treated with some of the chlorine gas from the nickel cells, in order to oxidize the ferrous chloride of ferric chloride. By means of sodium hydroxide the iron was then removed from the solution. After the removal of the ferric hydroxide, the solution is a mixture of $NiCl_2$ and NaCl, and was then evaporated. In this way it was brought to such a concentration that the total sodium chloride separated out. The solution then contained only $NiCl_2$, and while still hot, it was flowed into the nickel electrolyzers. In these cells nickel was deposited on the cathodes and chlorine released at the anodes;

$$NiCl_2 + \text{electric current} = Ni + Cl.$$

The chlorine so produced was conducted to the shot tower to react with more of the copper-nickel alloy. The solution as it became impoverished in nickel chloride was returned to the evaporator.

The nickel cells were made of concrete and the multiple system was used, as in the copper cells. They differed from the latter in size and in the use of a porous diaphragm. As the electrolyte was more concentrated, the size of the cells was 2.37 meters in length, 71.5 cm. in width, and 40 cm. in depth. The cathodes consisted of strips of nickel of 28 cm. in length and 14.7 cm. in width; several such strips being suspended side by side from a conducting rod across the cell. Opposite to each series of nickel cathodes there was provided a series of Acheson graphite anodes, each being surrounded by a porous clay cylinder, without bottom, and of oval cross section; the short axis of the ellipse, perpendicular to the surface of the electrodes, was 8.75 cm. long, and the long axis 16.25 cm. These clay cylinders nearly reached to the bottom of the cells although some space was left between their lower ends and the bottom, in order to make a free circulation of the electrolyte possible. These porous diaphragms prevented successfully any chlorine from passing to the cathodes and diminishing the current efficiency. The efficiency was very good; during a period in which 10,000 kg. of nickel were produced it was in the average 1.029 gr. Ni per ampere-hour, *i.e.*, 93.5 per cent. of the theoretical current efficiency. The upper ends of the porous cylinders were connected to a cross tube of pottery ware, with an asphalt coating through which the chlorine was led off.

Nearly all of the chlorine was led to the tower containing the nickel-copper shot; only a small portion was used to convert the ferrous chloride into the ferric chloride. The consumption of power in the nickel-depositing cells was much greater than in the copper-depositing cells. The voltage at the terminals per nickel cell was 3.5 to 3.6 volts; there was also some loss of voltage in the conductors and contacts so that about 5.3 h. p.-hours were required per kilogram of nickel deposited. These figures were deduced from the following data representing a test of the operation in 1902. There were consumed during the test 52,524 h. p.-hours; duration of experiment 679 hours; average current 896 amperes; total ampere-hours 608,384; number of cells during the greater part of the time 16, and during a short period 15, the average being 15.97. As the cells were connected in series, the theoretical amount of nickel deposited would be equal to the product of the number of cells (15.97) the number of ampere-hours (608,384) and the electrochemical equivalent of bivalent Ni in grams per ampere-hour (1.09); this would give 10,590,000 grm. or 10,590 kilogrm., while the amount of nickel actually deposited was, 9,898.9 kg. or 93 1/2 per cent. of the theoretical amount; the actual consumption of power was 5.3 h. p.-hours per kilogram.

The difference of the power consumed in the deposition of the copper and the nickel is considerable. The weight of the copper deposited from Cu_2Cl_2 per ampere-hour is about twice that of nickel deposited from $NiCl_2$ per hour, while the actual voltage is 12 times smaller for the copper

than for the nickel, hence the energy required for the deposition of the copper in this process is 24 times smaller than for nickel for equal weights of deposits. The nickel deposited in the Browne process had excellent mechanical properties and was of high purity.

The electrolyte for the process was produced in the tower which contained a quantity of copper-nickel shot of the same weight as the anodes, for this purpose chlorine was supplied from the nickel-depositing cells and the sodium chloride from the evaporator; a proper quantity of water and a small quantity of hydrochloric acid was added. The shot is thus dissolved and the solution was supplied to the copper electrolyzers. An addition of hydrochloric acid was necessary, because some additional chlorine was required for the formation of the electrolyte, while hydrogen escapes. This may be made clear from the following considerations.

After the solution has passed out of the copper-depositing cells, sodium sulphide is added, the sulphur combining with the copper of the cuprous chloride, while the sodium remains as sodium chloride in the solution. Later sodium hydroxide is added, the iron is precipitated as hydroxide, while new sodium chloride is formed in the electrolyte. Hence, in two steps of the process, sodium is substituted for copper and the iron in their chloride solutions. If in the evaporator, all the sodium is separated from the solution, its quantity will be somewhat greater than the amount of sodium chloride which was supplied to the shot during its solution in the beginning of the process. This surplus of sodium chloride comes from the sodium, which was added in the form of sodium hydroxide and sodium sulphide, and from the chlorine ions which were present, and the chlorine undergoes a cyclic process partly free and partly in combination, it follows that there would be a deficiency of chlorine at the end of a cycle if a quantity of hydrochloric acid was not supplied to the shot, equivalent to the amount of sodium in the added quantities of sodium hydroxide and sodium sulphide. These quantities are small because the amounts of cuprous chloride after the solution has left the copper-depositing cells, and the amount of iron in solution are small. Hence only a relatively small amount of hydrochloric acid is required.

Browne found that in electrolyzing a hot nickel chloride solution, free from sulphates, the Acheson graphite anodes proved so excellent that their corners and edges remained sharp after two or three years.

Sjostedt-James Process.[1]—This process consists in dissolving the copper and nickel with sulphuric acid, electrodepositing the copper with insoluble anodes, then making the solution ammoniacal, separating the iron by air blast, and finally depositing metallic nickel from the heated bath.

The ore is treated for 8 or 10 hours with 40 per cent. sulphuric acid at

[1] U. S. Patent 725,998.

the boiling-point. Copper is deposited, using copper cathodes and insoluble anodes, and a current density of 0.3 amperes per square decimeter, the electrolyte being agitated by a current of air. When the solution is sufficiently concentrated in nickel, the copper is completely separated by filtering through a bed of iron sulphide or nickel sulphide. The solution is nearly neutralized with caustic soda, then rendered ammoniacal, and the iron precipitated by an air blast. The nickel is then deposited from the resulting neutral or slightly ammoniacal solution, with insoluble anodes, and nickel cathodes, the solution being agitated and heated by a blast of hot air. During the decomposition of the nickel, a current density of 0.6 to 0.9 amperes per square decimeter is maintained.

The Gunther-Franke Process.[1]—In this process the ore is smelted to a copper-nickel matte which is then ground, and brought in contact with chlorine either in the form of gas, or in its nascent state, whereby the metallic sulphides are converted into the corresponding chlorides; after which the pure metals are electrolytically separated.

If the chlorine is used in the form of gas, the ground matte is introduced into a closed drum together with the solution of a chloride, such as sodium chloride, calcium chloride, magnesium chloride, or copper chloride, and treated with chlorine gas. The reaction which takes place if the temperature is not too high, is to convert the sulphides of the metals into the corresponding chlorides or sub-chlorides, while at the same time sulphur is set free. Under practical conditions more or less of the sulphur contained in the copper-nickel matte is not obtained in its free state, but in the form of sulphuric acid. In order to reduce the quantity of sulphuric acid it is necessary to take care that the temperature is permanently kept at an invariable point.

The metals contained in the copper-nickel matte, being converted into the form of chlorides, the solid particles are separated from the solution and the solution is freed from sulphuric acid and other impurities so that, technically speaking, a pure nickel-copper solution is obtained. This nickel-copper solution is electrolyzed with insoluble anodes. Copper is deposited at the cathode while at the anode chlorine is liberated. The chlorine may be used for treating new portions of copper-nickel matte. The electrolyte becoming poorer in copper during the electrolyzing process, fresh copper-nickel solution is added till the contents of the bath in nickel is raised to a certain desired concentration. The bath is then freed from copper preferably by electrolysis and by precipitating the last traces of copper chemically, as for instance, by metallic nickel. The solution purified from copper and forming then a solution of chloride of nickel is then electrolyzed with insoluble anodes. In this electrolytic process chlorine is again set free and may be used for treating fresh portions of the copper-nickel matte. The nickel is deposited on the cathode.

[1] U. S. Pat. 876,633, Feb. 18, 1908.

The matte residue separated from the solution after the chlorine treatment consists substantially of sulphur and small portions of sulphides. The sulphur may be separated from the matte particles, and the matte particles may then again be treated with chlorine.

If it is intended to use the chlorine in the nascent state for treating the copper-nickel matte, the matte is used as anode in an electrolyzing process in which the electrolyte is formed of a hydrochloric acid solution of copper chloride in mixture with an alkali metal chloride. The cathode is a sheet of pure copper. In such an electrolyzing process chlorine is produced at the anode which converts the sulphides of the metals into

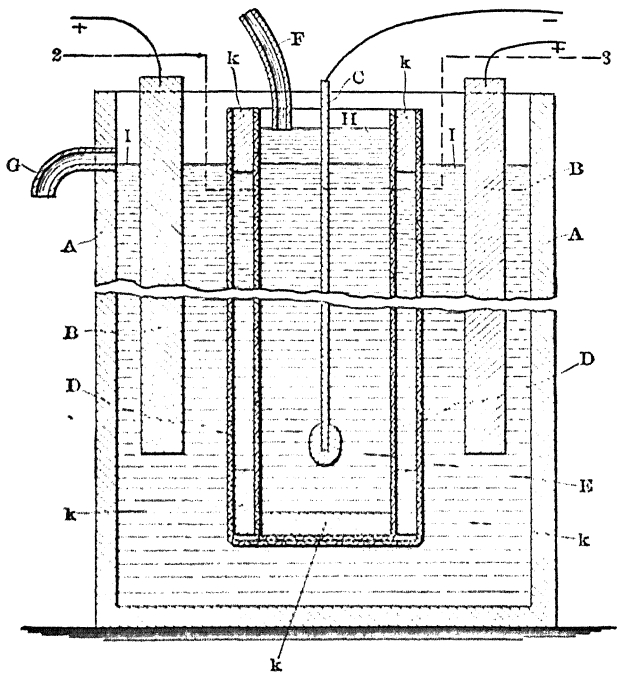


FIG. 68.—Hybinette process—electrolyzer.

the corresponding chlorides, at the same time liberating sulphur. The chlorine at the anode is entirely used for bringing metal into solution.

In view of the fact that more copper is deposited at the cathode than goes into solution at the anode, it is necessary to introduce a corresponding amount of copper salt into the bath. The nickel accumulates in the solution, and when sufficiently concentrated, it is purified, and the nickel deposited with insoluble anodes.

The Hybinette Process[1]—In the Hybinette process, the copper-nickel ore and matte is first converted into a crude copper-nickel alloy, and

[1] U. S. Pat. 805,969, Nov. 28, 1905.

this alloy electrolyzed in a sulphate solution. Fig. 68 shows the electrolyzer employed in the process, in which *I* is the electrolyzer, which is preferably a wooden tank lined with lead. It has an overflow *G*, which always keeps the level of the solution at *I* and contains a filtering bag *D*. The filter bag is made up of the wooden frame *K*, and two thicknesses of cotton cloth *D*, separated by the wooden frame *K*. *C* is the cathode plate with the wooden rib *E*, which is shown in the drawing to extend over the bottom edge of the cathode; but it may for still better protection extend all around the plate. *B* represents the anodes. *F* is the inflow, which is regulated in such away that the solution in the bag stands at the level *H*, which is about 1 in. above the level 3. The rib *E* prevents the cathode from warping and making contact with the bag.

In separating the copper and nickel, Hybinette employs as electrolyte a dilute solution of sulphate of nickel with a small proportion of weak acid—such as phosphoric acid, boric acid, lactic acid, or other organic acid.

The first step in working the process consists in placing in the electrolyte an anode composed of the alloy to be separated and a cathode-plate upon which the metal is to be deposited, and separating the electrodes by a pervious diaphragm, such as filter cloth. This is done by enclosing one of the electrodes, preferably the cathode, in a cloth bag. The cloth bag or diaphragm is so porous that if it were alone relied upon to separate the anolyte from the catholyte, the solutions would mix and become homogeneous in a short time. Its action is therefore supplemented by keeping the solution in motion, causing it to flow from the cathode to the anode through the porous material, and thus preventing the metal which has been dissolved at the anode from coming in contact with the cathode.

The anode may consist either of a pure alloy of copper and nickel, containing say equal parts of these metals, or containing them in other proportions, with considerable amounts of impurities such as sulphur, iron, carbon, silicon, etc.

The cathodes consist of copper plates, made of heavy metal—say 0.10 to 0.15 in. thick—held by a non-conducting, wooden frame. These thick metal plates when held in the frame will not warp and come into contact with the diaphragm, which would interfere with the process. To make the diaphragms more reliable, two thicknesses of cloth are used, at a distance apart of about 1/2 in. The electrolyte is caused to flow into the bag and through the filter cloth at right angles to the surfaces of the electrodes to the anode side of the tank. The rate of flow is easily regulated by maintaining a desired difference of level between the anode and cathode compartments. A constant flow of the nickel sulphate is supplied to the cathode-bag, and although deposition is going on,

the solution standing in the bag does not become deprived of its nickel, and thereby acidulated. The operation goes on continually, nickel being deposited at the cathode until a sufficiently thick plating has been made, when the cathode plates are removed and the nickel stripped therefrom, and there is a corresponding simultaneous solution of the copper, nickel, and iron at the anode until the anode is dissolved, when it is replaced by a fresh anode of impure alloy.

The second step of the operation is to remove the dissolved iron and copper from the liquid which flows from the electrolytic tank. The copper is precipitated on pure nickel slabs with solution kept at boiling temperature.

The iron is removed by passing the solution through an electrolytic tank containing insoluble anodes of platinum, lead or carbon, by which the iron compound is converted by oxidation from the ferrous to the ferric condition. The solution is then passed into a tank where nickel carbonate is added to it in excess. This precipitates the iron as carbonate, and it is then recovered from the solution by filtering. The solution is then returned to the bags, or cathode compartment, of the electrolyzers.

The process is therefore continuous; the nickel electrolyte being supplied to the porous bags in a continuous stream, so as to maintain an outward current from the cathode, the equivalent of copper, nickel, and iron being dissolved in the liquid on the anode side. The liquid thus treated is regenerated by cementation on slabs of copper or nickel free from carbon, silicon, and sulphur. The iron is then extracted from the solution, preferably by oxidation and precipitation, and the liquid thus regenerated and purified is again supplied to the electrolyzers.

Cito Process.—In a paper read before the Pittsburg meeting of the Electrochemical Society, May, 1910, Camillo C. Cito of the Irvington Smelting & Refining Works, describes[1] a new process for the treatment of copper-cobalt-nickel ores, rich in silver and arsenic, by combined smelting and electrolytic operations.

In this process the ore is smelted, without any preliminary roasting, in a reverberatory furnace with a quantity of copper and the necessary amount of the usual fluxes.

The addition of the copper practically eliminates arsenic from the fumes in the smelting process because the arsenic is absorbed by the copper.

Only two products result from this smelting process:

1. *An alloy*, containing besides copper, all the silver, nickel and cobalt, and nearly all the arsenic. On account of the subsequent electrolytic refining of this alloy, it is important that the different metals composing it should be present in a certain proportion, viz., it is necessary that: (a) The percentage of copper be two-thirds that of the nickel and

[1]See also U. S. Patents 522,475 and 532,080, Feb. 15, 1910.

cobalt, but (b) at least the same as that of the arsenic, and preferably not less than that of the silver. The alloy is tapped from the furnace directly into anode moulds. Besides the alloy there is obtained:

2. *A slag*, containing a very low percentage of silver, nickel, and cobalt. This slag can be used to advantage as a flux in the blast furnace, where the last traces of the metal can be recovered.

For instance, when smelting 174 lb. of the ore with the proper amount of copper and the necessary fluxes, no fumes were visible. The result of the smelting is to be seen in the following table:

TREATMENT OF COPPER-NICKEL ORE AND MATTE

	Canadian ore before smelting 174 lb.	Alloy after smelting 195 lb.	Slag after smelting 56 lb.
Silver	6200 oz. per ton	5500 oz. per ton	20 oz. per ton
Arsenic	12.5%	10.75%	trace
Nickel and cobalt	31.0%	27.5%	0.5%
Lead	none	none	none
Copper	none	19.5%	0.5%
Iron	3.5%	0.5%	7.6%
Sulphur	1.0%	1.2%	
Insoluble	9.64%		

All the valuable metals pass into the alloy; only a small fraction of the silver appears in the slag (20 oz. per ton). The data concerning the arsenic is noteworthy; 174 lb. of raw ore containing 12.5 per cent. arsenic, after the smelting, yields 195 lb. of alloy containing 10.75 per cent arsenic; allowing for the small error in analysis, it results clearly from these figures that no arsenic has escaped in the fumes.

The Electrolytic Process.—The different metals of the alloy are separated from the anode in an electrolytic bath by the electric current. The electrolyte consists of a solution of copper sulphate in water, which during the whole of the electrolytic process contains at least 10 grm. of copper and 5 grm. of free sulphuric acid per liter.

The cathodes are sheets of pure copper.

The density of the current has to be regulated according to the composition of the anodes and electrolyte and according to the temperature.

The temperature is kept advantageously at 60° C. or higher, and is otherwise regulated by the percentage of arsenic in the anodes. In case proper conditions prevail, viz., if the electrolyte as well as the temperature and the electric current correspond to the composition of the alloy, the following results will be obtained:

1. The copper contained in the anode is deposited in the form of pure electrolytic copper on the cathode.

2. The silver of the anode is quantitatively precipitated in the slimes.

3. All the nickel and cobalt dissolved from the anode remains in solution in the electrolyte.

4. At the proper temperature the larger part of the arsenic is found dissolved in the electrolyte, the balance going into the slimes with the silver.

The copper deposited on the cathode is exceedingly pure. A determination of the copper yielded 99.89 per cent. Cu.

The slimes, of course are rich or poor according to the percentage of silver in the anodes. Under all circumstances the slimes contain all the silver in the anodes, as neither in the cathodes nor in the electrolyte can traces of silver be determined. The small quantities of arsenic which go into the slimes, together with the silver, can be easily removed by a light roasting or dissolving process. The slimes can then without any difficulty be refined by the usual cupelation process.

The Electrolyte, containing the whole of the nickel-cobalt and larger part of the arsenic can be brought up to the following concentrations:

Silver,	None.
Copper,	10 grm. per liter.
Nickel-cobalt,	55 grm. per liter.
Arsenic,	30 grm. per liter.

By using insoluble anodes almost all the copper contained in the electrolyte can be precipitated as pure copper on thin lead cathodes. The density of the current can be lowered according to the decrease of the copper in solution, and at the same time the temperature can be raised. With a current density of 150 to 200 amperes per square meter and a temperature of 80° C. the copper in the electrolyte can thus be reduced to about 2 grm. per liter.

The precipitated copper is very smooth, and can be detached from the lead sheets and used as cathodes in the regular electrolytic baths.

The remainder of the copper is advantageously precipitated by hydrogen sulphide in the cold, whereby very little sulphide of arsenic is formed. This copper product can be used as a flux.

All the arsenic can then be precipitated by hydrogen sulphide upon heating as practically pure sulphide of arsenic, which can be placed on the market as such.

Nickel and cobalt can now be recovered, together or separately, by any of the methods usually employed, such as electrolysis or chemical precipitation.

PROCESS USED AT KRUGHUTTE, MANSFELD COPPER CO.

A new process is mentioned in *Metallurgie* of Jan. 8, 1908; it is being tried at the Krughutte, near Eisleben, of the Mansfeld Copper Co. The object is to avoid the silver loss during the bessemerizing of copper matte and to avoid also the troubles of the effect of sulphur fumes on vegetation. It has been found that in bessemerizing copper matte the loss of

silver increases during the progress of the operation and reaches a maximum after the sulphur and iron have been removed. Only when a concentration of 79 to 80 per cent. of copper has been reached, the loss of silver sets in. It is, therefore, proposed to stop with bessemerizing when the copper matte contains between 72 and 76 per cent. of copper. This is then to be treated directly by electrolysis by a process of the Metallurg Ges. in Frankfort.[1] The sulphur is removed by electrolysis and obtained in elemental form. Silver, sulphur, nickel, etc., may be easily and completely recovered from the anode slimes. The cathode copper is claimed to be as good as any electrolytic copper. The process is being tried practically on a large scale in a plant for a yearly production of 600 tons of electrolytic copper, and has been in use since the middle of Feb., 1907. It is claimed that the process has so far proved technically reliable on a large scale.

[1] German Patent 160,046, Oct. 5, 1904.

CHAPTER XVI

PRECIPITATION OF COPPER FROM MINE WATERS

The precipitation of copper from mine waters dates back to the fifteenth or sixteenth century. It is referred to in the writings of Paracelsus the Great who was born about 1493 and died in 1541[1] as follows: "For truly when the rustics in Hungary cast iron at the proper season into a certain fountain, commonly called Zifferbrunnen, it is consumed into rust and when this is liquefied with a blast-fire, it soon exists as pure Venus (copper), and nevermore returns to iron. Similarly in the mountain commonly called Kutenberg they obtain a lixivium out of marcasites, in which iron is forthwith turned into Venus of a high grade, and more malleable than the other produced by nature."

It is also referred to by Basil Valentine, who wrote about 1500; it was in practice in the Lower Hartz until the middle of the sixteenth century; it was in operation in Peru before the year 1637; it was patented and practiced at Rio Tinto as early as the sixteenth century.[2]

Since the precipitation of copper by iron was first discovered it has been used in various parts of the world. Its largest and most comprehensive development has been at Butte, Montana, since 1880, when it was discovered that the mine waters were sufficiently copper-bearing to warrant precipitation.

The weathering effect on cupriferous sulphide ores, is to convert the insoluble copper sulphide into the soluble copper sulphate. In large mines, which have extensive underground workings, the low-grade ore and waste material in the old stopes, through the combined action of air and water become oxidized and the copper, due to its own oxidation and the action of ferric sulphate, becomes soluble. A similar action takes place in old waste dumps. Frequently, also, as the result of underground fires, the sulphides are converted into sulphates, which render the copper soluble in the mine waters. The copper, once soluble, is readily precipitated with scrap iron.

In some of the older and larger mines, notably the mines at Butte, Montana, and the Copper Queen, Arizona, the precipitation of copper from the mine waters, has assumed enormous proportions. No less than 30 precipitating and waste dump leaching plants are in operation along the Silver Bow creek in East Butte, and the total output of precipitate,

[1] English translation by Arthur Edward White, Vol. I, page 28, London, 1894. Horace V. Winchell, *Min. and Scientific Press*, Feb. 24, 1912.

[2] W. G. Nash, *Mining and Scientific Press*, Feb. 3, 1912.

or cement copper, is about 750 tons per month. The product will average from 60 to 75 per cent. pure copper, and the monthly recovery is approximately 900,000 lb. Of this quantity about 80 per cent. is recovered from the copper-bearing mine waters, and about 20 per cent. from the water percolating old tailing dumps.

Precipitation of Copper from Mine Waters at Butte.—The precipitation of the copper, according to A. F. Bushnell[1] was first put on a business basis at Butte in 1901 by William Ledford, who secured a 3-year lease on the water of the St. Lawrence and Anaconda mines at a 25 per cent. royalty. During this lease the copper water became so strong that in a short time it ate up the pipes through which it was pumped to the surface, wherefore the companies weakened the water by passing it over iron underground. Ledford contested this on the ground that he was to have the entire right of precipitation, and sued the Anaconda company and was awarded a few thousand dollars damages.

After Ledford's successful venture the companies refused further lease, deciding to do their own precipitating. At the present time the operators of the various precipitating plants are the large companies themselves, down to the leasers and to the individuals who take the tail waters from the large operators and win from it a little of the remaining copper that will precipitate.

The Boston & Montana, an Amalgamated company, according to Stone[2] alone recovers 100,000 lb. of copper per month, and its operations show a profit over the entire pumping expense.

Great difficulty was at first experienced by the mining companies, to find something that would withstand the action of the mine waters on pumps and pipes and that would be within a reasonable cost. Phosphor-bronze castings were found to be necessary for the entire water end of all pumps where the water was found to be even slightly acid. The phosphor-bronze is composed of 93 per cent. copper, 0.5 per cent. phosphorus, 4.5 per cent. tin and 2 per cent. lead. This metal, however, was too expensive for pipes.

Flanged steel pipes with lead gaskets and lead lining were found to withstand the action of the water with a degree of satisfaction, but wood-lined pipe, which is less expensive, is now in practically universal use throughout the Butte district. For high-pressure water columns in shafts and other lower pressure pipes, a flanged steel pipe is used and the wooden lining forms a male and female connection at the joints.

The lining is composed of pine slats put in place with hot asphaltum

[1] *E. and M. J.*, June 29, 1907.

[2] Charles J. Stone, *E. and M. J.*, May 8, 1909.

and the key piece is fitted and driven in firmly, so that the lining is held tightly in place. The whole pipe lining is then carefully painted with asphaltum, and when the pipe is put in place, great caution is taken in packing the joints to prevent seepage. In shafts where water from the upper levels drips on the pipes, it has been found necessary to thoroughly paint and cover the pipes with canvas, and the canvas then receives a thick coat of asphaltum. Wooden, wire-bound pipes are also used underground for light service, and on the surface wooden launders are used.

The copper content as well as all other mineral salts and the amount of free acid in the mine waters, varies widely in different mines and different sections in the district. Cupriferous waters were not encountered to any great extent in the upper levels, nor at shallow depths, but when the shafts penetrated the great copper horizon at from 500 to 2200 ft. in depth, the waters were found to be highly charged with mineral salts and free acid.

Old workings, abandoned upper levels and gob or stope fillings that have long been exposed to the oxidizing influence of air and where waters leach through them, are productive of the highest grade of cupriferous water. When a deep level is opened, the flow is found to contain free acid, but only a small amount of copper sulphate is present. As the levels become opened and the decomposition of sulphides takes place, the water is enriched.

A flow coming from a section where the sulphide ore is burning or from a level where the fire has been extinguished, is remarkably enriched. The mine water of the Boston & Montana has been built up within a short period of time from this source alone from 0.02 per cent. copper content to above 0.2 per cent., and at this strength it threatened to destroy the phosphor-bronze castings of the pumps. For this reason an effort was made, where possible, to regulate the grade of water to a strength that will not attack the bronze pump parts.

The cupriferous water from the various mines carries from 0.01 per cent. to 0.031 per cent. copper as sulphate. It would appear that the mine waters are extremely poor in copper as compared with the solutions in a leaching operation, but when a mining company is pumping 500 gallons per minute, the precipitation amounts to approximately 1600 lb. of copper per day and the saving is effected with but little expense.

The copper precipitation is effected in open launders, and in towers. The launders are set at a sufficient grade so that the water flows rapidly, and scrap iron of all classes is thrown into it, but care is taken to allow the water to flow freely. The launders are from 3 to 4 ft. wide and from 1 to 2 ft. in depth, and are built single or double. The water is kept at from 6 to 12 in. in depth in the launders. If the water as it comes from the

mine is strong in acid, better results are obtained where the water flows at a greater velocity, but if weak in acid, a slower flow is desirable. It is well at all times to keep the iron and the launders free from accumulations of iron oxide.

The towers are built from 8 to 12 ft. wide, 10 to 14 ft. high, and from 50 to 150 ft. long, the size depending entirely upon the flow to be handled. They are built open on sides and ends and large scrap sheets of iron are placed to hold the dripping water within the water-tight bottom; or they are enclosed entirely on all sides by baffle-boards to keep all water within the tower sump. The water comes into the top of the tower in an open launder and the flow is regulated by means of gates and side distributing troughs so that the shower is uniform throughout the tower. The tower is filled with scrap iron for perhaps one-quarter to one-half its height.

Experience has shown that a better extraction is effected in the towers than in the launders. This is especially noticeable where the solution is both weak in acid and copper. Doubtless exposure to air has a beneficial effect, but the arrangement is more efficient in that the falling water keeps the scrap iron clean and bright, and prevents an accumulation of iron oxide slimes.

A clean-up is effected by turning the flow into other launders of the plant, scrubbing and washing the scrap free from copper scale and sluicing the launders and tower sump into settling tanks, where the clear solution is decanted off. The cement copper is then dried, barreled and shipped to Great Falls where it is smelted in reverberatory furnaces. The average quality of the precipitate is between 60 and 70 per cent. copper.

A well arranged plant is so located that the solutions can flow by gravity from the mine through the launders and down through towers, with the clean-up vats below. It is well to place the clean-up vats and dryer under the same roof. The extent or magnitude of the plant depends upon the limit of extraction it is found profitable to make from the solution. All launders and towers should be built in parallel duplicates so as to facilitate rapid and thorough cleaning. Wrought iron and steel scrap are better than cast iron and thin sheets are more satisfactory than heavy pieces. About 75 lb. of cement copper are recovered in practice from 100 lb. of scrap material.

A number of large tailings dumps from the early concentrating mills, which were neglected for years, are being worked successfully in connection with the precipitation from mine waters. The dumps carry approximately 1 per cent. of copper. Years of weathering have made possible the leaching of these tailings on a profitable basis.

The dumps are from 20 to 50 ft. in depth and cover many acres of ground. The dump, which is located in the bed of Silver Bow creek,

contains more than 200,000 tons of sands. They average from 20 to 30 ft. in depth.

The supposedly barren tail water from the precipitating towers of the Boston & Montana Company is elevated to the highest point on the dump. Ponds of from 5000 to 15,000 sq. ft. are arranged so that the over-flow from the higher will run to the next lower pond until the entire flow is absorbed. To reclaim the water after it has leached through the sands and taken up the soluble copper, two level tunnels were driven through the dump on the slime-covered soil of the valley and a cribbed trench surrounds the dump, all of which lead to a common sump to be elevated into the precipitating towers or flows by gravity into precipitating boxes.

The water which is fed to the ponds contains but a trace of copper and is very weak in free acid. After the leaching, its copper content has been built up to 0.02 per cent. and precipitation is satisfactory. The product from this particular plant averages 80 per cent. copper. 750 gallons of mine water are pumped per minute upon the sands and, approximately 80 per cent. of this is recovered and fed to the precipitating plant. A daily analysis of the leached solution gives a close estimate of the daily recovery of copper.

Bushnell gives the cost of recovering the copper from the Butte mine waters as 8 cents per pound.

According to Probert[1] the consumption of scrap iron at the Parrott Precipitating Plant at Butte is figured at 4 units of iron per unit of copper obtained.

The following method is used for leaching and precipitating at the Red Metal precipitating plant on the tailing dump of the Montana Ore Purchasing Company's old concentrating mill.[2] The original tailing carried about 1 per cent. copper and was deposited on a bed of slime which provides a very effective impervious stratum, preventing the loss of leaching water.

The dump is divided into two sections and has a total area of about 10 acres. The surface of each section is arranged in terraced ponds, into which the leaching water is pumped by means of Morris phosphor-bronze centrifugal pumps. On the larger section, one 20-h. p. pump elevates about 700 gallons per minute to a height of 25 ft. Both pumps are motor driven and require but little attention. The leaching water used in this plant is mine water which has been previously treated in a precipitation plant where about 95 per cent. of its copper content has been recovered, leaving from 0.003 to 0.004 per cent. copper.

[1] *Min. and Scientific Press*, Jan. 4, 1908.

[2] *Mettallurgical and Chem. Eng.*, Nov., 1910.

ANALYSIS OF MINE WATER USED IN LEACHING

Constituents	Grams per liter
SiO_2,	0.0992
CuO,	0.0225
Al_2O_3,	0.1241
Fe_2O_3,	0.1541
FeO,	1.5082
MnO,	0.0502
ZnO,	0.4257
CaO,	0.3936
MgO,	0.2172
SO_3,	3.5400
Cl,	0.0234

The percolating water is collected in tunnels extending through the bottom of the dump, and is finally discharged into a sump where it is pumped to the precipitating launders. On the larger dump the tunnels are about 200 ft. apart and have an aggregate length of 1200 ft. They are 5 ft. high, 3 ft. wide at the top and timbered throughout. On the smaller dump there are about 800 ft. of tunnels. The number and length of tunnels is dependent on the nature of the ground on which the dump is formed. Porous ground which would permit heavy loss of water by seepage would require more collecting tunnels than an impervious foundation stratum. At the Red Metal plant the seepage loss amounts to about 20 per cent.

A section of the dump surface is allowed to dry out periodically, so that the accumulation of precipitated iron compounds may be removed and the dump material allowed to oxidize before further leaching. The rapid accumulation of iron compounds is due to the fact that the mine water used carries considerable iron from previous treatment, and on exposure to the atmosphere deposits the oxide and basic sulphate of iron. This accumulation prevents leaching and is occasionally scraped from the surface of the pond. By this treatment the dump yields a constant supply of copper, this particular dump having been leached continuously for 4 years with no apparent diminution in yield.

The leaching water collected through the tunnels carries from 0.015 per cent. to 0.03 per cent. copper. This is not as high grade as some of the mine waters, but is profitable. The launder system is preferred for precipitation rather than the tower system. The advantages lie in convenience of operation, particularly in charging the launders with scrap iron, and in cleaning up the copper precipitate. The launders are 4 ft. wide and 1 ft. deep. and preferably have a fall of 1/2 in. to 3 ft. Launders of this size and from 600 to 700 ft. long will serve to precipitate successfully 400 gallons of copper-bearing water per minute. At the Red Metal plant the launders are 700 ft. and 512 ft. long, respectively, on the larger and smaller dumps.

Scrap iron and tin cans are used for precipitation. Paper must be removed from the cans, and if greasy they must be burned before use. The Red Metal plant has about 75 tons of scrap in constant use; the launders are replenished with about 1000 lb. daily. Iron is consumed at the rate of 1 1/2 lb. for each pound of cement copper produced. The precipitated copper is swept from the iron every 2 hours during the day, and is carried to the sump by the stream of water flowing through the launders. Thus no handling of the iron is necessary after it has been placed in the launders. From the sump the copper is shoveled onto a drying platform and is shipped to the refinery with about 15 per cent. moisture.

The recovered precipitate assays about 75 per cent. copper and 8 per cent. iron, with smaller percentages of other impurities. About 90 per cent. of copper in solution is precipitated in the system described. The richer the solution the more efficient the precipitation. Scrap iron is paid for at the rate of $8.00 per ton, although as high as $12.00 has been paid when copper was selling for 25 cents. Payment for precipitates is made on the wet assay, less 1.3 per cent., and at 4 cents less than the market price for copper.

Power costs $6.00 per horse-power-month. Labor cost is low, as two day laborers and one night watchman only are required at the Red Metal plant, in addition to the superintendence.

According to Floyd Bushnell[1] a test made with the same water shows that tin cans produce a 33 per cent. copper precipitate, and iron 50 per cent. The operators sell their output to the smelters at 4 cents less than the market quotation for copper; the shippers must pay a treatment charge of $5.00 per ton. Because of the increased demand for scrap iron for precipitation purposes during the past 5 years the price of old iron has increased from $7.00 to $12.00 and $14.00 per ton; $10.00 is the average price for a ton of tin cans.

The Boston & Montana plant at Meaderville, is one of the largest and most up to date in the district. Two flumes, 1000 ft. long and 4 1/2 ft. wide, 800 lin. ft. of boxes, and four large towers are operated by this company. The towers are 100 ft. long, 30 ft. high, and 6 to 8 ft. wide. The lower towers have two electric elevators to raise the iron to the top of the towers. The precipitate is dried to 8 per cent. moisture, barreled, and shipped in 30-ton lots to Great Falls for treatment; three shipments per month is the average output. The average strength of the Boston & Montana copper water is 0.05 per cent. But during the fire that raged several years ago in the underground workings, the percentage of the water ran as high at 0.32 per cent. Under normal conditions the precipitate averages 60 per cent. copper. An assay of the cupriferous

[1] *Mining and Scientific Press*, Nov. 18, 1911.

waters after it passes the last precipitating plant in the district shows the exceedingly small percentage of 0.0002 copper.

In the plant of the Original mine, one of the most economical in Butte, three men take care of 1400 lin. ft. of boxes. This company was the first to use the hose-washing system, which is decidedly effective. City water, under good pressure, is piped to all parts of the boxes, and at regular intervals the precipitate is washed from the half-eaten metal and from the bottom of the boxes. The precipitate is protected by means of a shelf, 2 in. from the bottom, and once it is separated from the metal, is unimpeded in its course to the settling tanks. The system is so arranged that the copper water may be shut off from any part of the plant. The high-grade precipitate is flushed into tanks $2\times7\times9$ ft. in a steam-drying room. There are two tanks, each holding 21 tons and are filled several times per month.

Precipitation of Copper from Mine Waters at the Copper Queen Consolidated Mining Company, Bisbee, Arizona.[1]—In the older mines belonging to this company, the Czar and Holbrook, where the ore zone extends from the surface to a depth of 500 ft., the ore near the surface is highly oxidized and the mine water contains considerable copper. At the deeper mines, the Gardner, belonging to the Copper Queen, and the Irish Mag, belonging to the Calumet and Arizona company, where the ore-zone lies from 600 to 1110 ft. below the surface, the mine water contains much less copper, while at the Cole shaft of the Superior and Pittsburg company, where the ore bodies are much deeper and more widely scattered, the copper in the water is almost negligible. The only mines where the water contains enough copper to pay for recovery are the Czar and Holbrook. The water at the Holbrook is pumped from the 500- to the 400-ft. level and flows to the Czar shaft, where it is raised to the surface with the water from the Czar mine. The amount of water pumped at this shaft is approximately 300 gallons per minute, averaging about 10 gr. of copper per gallon. All this water flows through the precipitating plant.

The precipitating plant consists of five tiers of troughs on three sides and four tiers on the other side, forming a rectangle, the outside dimensions of which are 78×108 ft. The troughs, which are made of 2-in. planks, are of rectangular cross section, 3 ft. wide by 20 in. deep. In the troughs, at intervals of 2 1/2 ft. are 2×4-in. cross-pieces raised 2 in. above the bottom; lengthwise on these cross-pieces are laid four 1×4-in. boards. This arrangement leaves a place for the copper to deposit until washed down into the settling tanks. In each tier there are two sets of troughs set side by side. These join together at each corner so that all the water can be made to flow through one while the other is being cleaned. The troughs are supported by 8×8-in. posts and 6×8-in. stringers. The tiers are 6 ft. apart vertically, making the total height

[1] *E. and M. J.*, Oct. 31, 1908, W. H. Chittenden.

of the structure about 30 ft. The slope of the troughs is from 1/4 to 2 in. per 12 ft. increasing gradually through the successive tiers.

The water enters at one corner of the upper tier, and flows through the two troughs around the rectangle to the corner where it entered. At this point the water passes down a slide and flows in a similar manner through the successive tiers, until at the end of the last tier it flows into a flume. This flume takes the water to settling tanks, $17 \times 9 \times 9$ ft. deep,

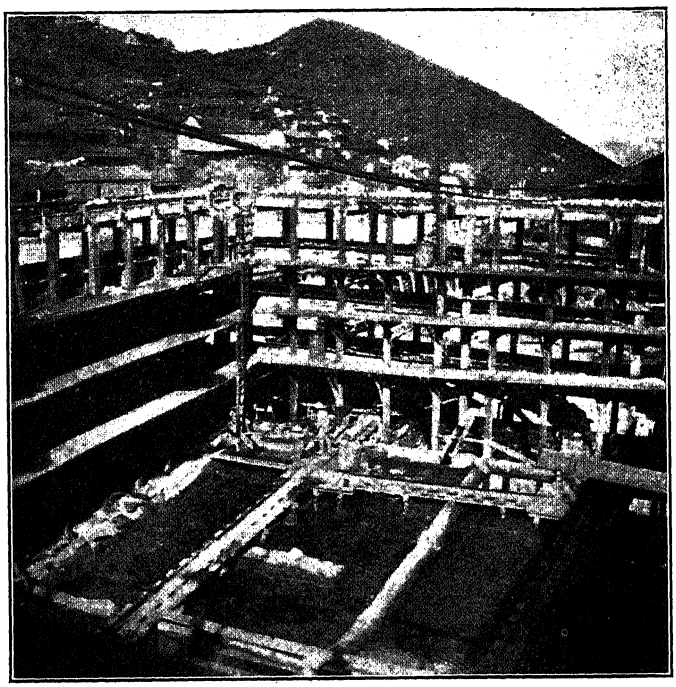


FIG. 69.—Copper Queen precipitating plant. Interior view.

a few hundred yards below the plant. These last tanks catch a small amount of the finest particles of copper and slime suspended in the water coming from the main plant. The total average length that the water flows in the troughs is about 1650 ft.

The precipitation is effected by means of tin cans which loosely fill all the troughs of all the tiers. Scrap iron is used to a small extent, but the results are much less satisfactory than with the cans, principally because of the greater surface exposed by the cans. The precipitate is a thick yellow material containing in addition to copper, the replaced iron, some little silica, unconsumed fragments of can, etc.

In the upper tiers the clean-ups are made every second day, but less frequently in the lower tiers, owing to the smaller amount of copper

precipitated. While collecting the copper the flow of water is shut off from one trough at a time. This trough is then drained and the cans washed thoroughly with water from a hose under pressure. The water, containing the copper product, is run into settling tanks where in about 2 hours the metal settles sufficiently so that the water can be siphoned off. After these clean-ups, occurring every other day, more cans are added as required. Once a month each trough is emptied and a thorough

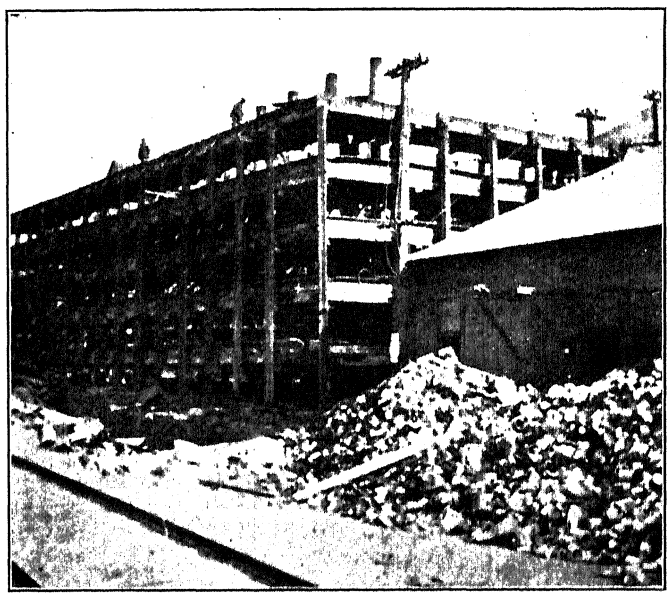


FIG. 70.—Copper Queen precipitating plant. Exterior view.

clean-up made. The troughs are then refilled with a new supply of cans.

The clean-up settling tanks, of which there are four placed in the interior of the rectangle, are 25×40×2 ft. deep. Once a month these tanks are cleaned out; the wet mud is bailed up in buckets, emptied into a car and dumped into a drying tank, where it remains for about 1 month before being shoveled up and loaded into the railroad cars, to be taken to the smelter at Douglas. There are two of these drying tanks 18×25×2 ft. deep.

The cans which are collected in Bisbee are contracted for at a nominal price per ton. Mexican labor is used entirely, the amount required being very small, as only two men are working steadily. For cleaning out the settling tanks, three extra men are required 4 or 5 days a month. The precipitate handled by these three men is loaded, when dry, by five others into a railroad car, holding 45 tons, in 1 day. The product when shipped contains about 40 per cent. moisture; the dried samples

assay 35 per cent. copper; 6 per cent. silica; 17 per cent. iron; 13 per cent. alumina; and 1.5 per cent. sulphur.

The saving in the plant is high, averaging more than 90 per cent. of the copper in the water. The highest extraction is obtained when the flow of water is low, and it is possible that it is obtained at the expense of excessive iron consumption. When the flow of water is greater the extraction is somewhat less.

Precipitation of Copper from Mine Water at the Ashio Mine, Japan.[1]—At the Ashio copper mine of the Furukawa Mining Co., in Japan, the mine waters are run over scrap iron, precipitating most of the copper as cement copper, and leaving iron sulphate with some copper sulphate in solution. This water is then used in the concentrators, after which it is run into a river for irrigating rice fields. Consequently, it is necessary to clarify the water before it is discharged. The discharge amounts to about 600 to 700 cu. ft. per minute, and averages about 0.00025 per cent. of copper. The water is run through three settling ponds, in the first of which slime and sand settle. In the second and third there is a slight precipitate of metallic hydrates, carrying some copper and slime high in silica. The copper in this deposit runs from 0.5 to 1.0 per cent. In the fourth pond milk of lime is then run in, in quantities from 10 to 20 per cent. of the amount required for complete neutralization and precipitation of the sulphate in the water. This causes a precipitate to settle which is mostly hydrated iron oxide and free from copper. The iron precipitate also carries down with it most of the colloidal slime in suspension, consisting mostly of alumina and silica. The water is then run into a fifth pond, where the lime necessary for complete precipitation is added. This precipitates the metallic hydrates completely, the precipitate settling in this pond in a sixth, from which it is run over a sand filter before it is discharged. The average of three analyses on the precipitate in the fifth and sixth ponds was as follows: Cu, 5.78 per cent; Fe, 12.91 per cent.; CaO, 6.76 per cent.; Al_2O_3, 4.70 per cent.; Mn, 4.40 per cent.; SiO_2, 11.25 per cent.; loss on ignition, 30.90 per cent. This precipitate is rich enough to be smelted. The process saves about 18 tons of copper per month and gives a clear waste water which is not injurious to agriculture.

Leaching of Copper Ore in Place.—In abandoned mines, once extensively worked, it is evident that the decomposition of the ore too low grade to work may take place indefinitely, and result in the production of cupriferous water from which the copper may be profitably recovered. The decomposition of the iron sulphides results in the formation of sulphuric acid and ferric sulphate, both of which are capable of acting on the various copper minerals. The seepage from the various mine workings gravitate toward the sump, where it may be pumped out, the copper

[1] J. W. Richards, New York meeting of the A. I. M. E., Feb., 1912.

precipitated, and the water again returned to the upper levels of the mine if there is not sufficient water from natural drainage. There are several instances in which abandoned copper mines have been profitably worked by pumping and precipitating the mine waters.

Attempts have been made to imitate this natural process of leaching *in situ*, and while successful working has not yet been accomplished, results have been encouraging. It is necessary that the material to be leached should be porous and permit of reasonable penetration of the water. The distance apart of the levels will largely be determined by the porosity of the ore. The deposit may be developed as in the exploration of a mine, in which the workings all lead to a sump to which the percolating water flows and from which it is pumped, precipitated, and if desired, again used to flood the upper levels.

CHAPTER XVII

REFINING OF COPPER PRECIPITATE

In the chemical processes the precipitate is usually in the form of cement copper, containing more or less impurity. In the electrolytic processes the precipitated metal is of great purity so that the ordinary fusion refining, incidental to casting it into ingots, will be quite sufficient to bring it to the state of the best refined or electrolytic copper.

Cement copper is a mixture of the metal, with iron, graphite, basic salts, usually a little silica, and sometimes arsenic, antimony, and the arsenate of iron.

The cement copper, when treated in connection with smelting plants, is usually charged into the smelting furnaces with the regular charges of ore, or into the converters and blown, with the matte, into blister copper.

At the Gumeshevsky mine, in Russia, the cement copper, containing 60 to 70 per cent. of the metal, is treated by melting it in a reverberatory furnace, adding to it a small quantity of matte of the grade of white metal to remove impurities. The resultant blister copper is then rabbled and poled in the usual way to produce a brand of the best selected metal.

At the works of the Chicago Copper Refining Co., the higher grades of cement copper, containing from 70 to 75 per cent. of the metal, is put into the refining furnace along with the blister copper. The oxide of copper contained in the cement copper is reduced largely by the sulphur from the blister and the charcoal in the refining furnace, and the silica and iron impurities go off as slags.

The precipitate obtained from the neutral chloride of iron solutions at Phoenixville and at Ore Knob, as well as that obtained by the Hunt and Douglas process from cuprous chloride, contained absolutely no deleterious substances and was charged directly into the refining furnace without other mixture.

At the plant of the Arizona Copper Co. at Clifton, Arizona, the cement copper averages 72 per cent. Cu. It is moulded into large bricks, by hand. After sun drying for a month the bricks are sufficiently dry to be fed into the copper converters, in connection with the smelting plant.

At Falun, Sweden, the cement copper is smelted and granulated for conversion into copper sulphate, by means of dilute sulphuric acid, in the ordinary way. The residual mud from the copper sulphate

crystallizers containing gold, silver, selenium, and bismuth, is dried and smelted with litharge, soda, and sawdust, to collect the precious metals into lead.

At Stadtberge, the cement copper is washed in wooden drums 10 ft. long and 4 ft. diameter, provided inside with wooden cleats arranged in spiral, through which passes a stream of water in the opposite direction to that taken by the cement copper; the escaping slimes are caught in settling tanks. The classified product consists of two-thirds of pure cement copper containing from 90 to 95 per cent. of the metal, and one-third slimes containing from 10 to 25 per cent. The cement slimes are agglomerated with slacked lime and smelted for black copper in a cupola furnace. To 3 tons of the prepared slimes 1/2 ton of refinery slag is added and 1/2 ton of slag from previously smelted slimes. The black copper thus produced is refined together with the washed cement copper in a refining furnace fired with gas. The charge is 2 1/2 to 3 tons of cement copper and 1 1/2 to 2 1/4 tons of black copper, which is treated in 24 hours, with a consumption of 3000 to 3500 lb. of coal and 250 to 300 lb. of charcoal. The argentiferous copper is cast into anodes and then refined electrolytically.

At Rio Tinto, Spain, the crude precipitate, containing about 70 per cent. copper, is thrown, a little at a time, on a perforated plate at the head of a long launder or tank and is washed through the plate by a strong stream of water from a small nozzle. The material that does not pass through the screen consists of leaf-copper and small pieces of iron; this material is thrown into a heap and afterward sorted over by girls who remove the pieces of iron. The precipitate that passes into the launder, is repeatedly turned over against the stream of water and by this simple means a concentration is effected.

The first few yards of the launder contain a red precipitate known as "No. 1 precipitate," containing 94 per cent. copper and less than 0.3 per cent. arsenic; following this is "No. 2 precipitate," containing 92 per cent. copper and between 0.3 and 0.75 per cent. arsenic, while below is the "No. 3 precipitate"; this is in a state of very fine division and contains on an average 50 per cent. copper and 5 per cent. arsenic. This last-named portion, which carries all the graphite from the pig iron, contains the bulk of the antimony and bismuth that is also precipitated from the liquors. Classes No. 1 and No. 2 are shipped to the refinery. The No. 3 precipitate is moistened with acid liquors, made into balls by hand and dried in the sun. These balls become cemented hard and are taken to the smelter, where they form part of the charge for the blast-furnaces and are run down to matte to be subsequently bessemerized, thus effectively removing the arsenic, antimony, and bismuth they contain.

Very impure cement copper may be smelted for matte with the

addition of high-grade raw ore. If the copper contains a large amount of carbonaceous material, such as the precipitate produced with sponge iron, the copper is first heated to redness to burn out the carbon. In doing this, a considerable portion of the copper is oxidized. Such a treatment is also beneficial if the cement copper contains large quantities of arsenic, which is thereby removed in the form of arsenic oxide.

Encouraging results have been obtained by the author in refining cement copper direct electrolytically, without passing through the stage of fusion.

Whatever the method used to get a high-grade copper, it will be necessary, or at least desirable, to cast the copper into the form of convenient ingots. While this is being done, the copper may undergo the regular process of fusion refining. This is universally done in two stages:

First: Subjecting the molten copper to the oxidizing action of the air, to eliminate and slag off impurities, and

Second: Reducing the oxide of copper formed in the process, back to the metallic condition after the impurities have been oxidized and eliminated.

Oxidizing Stage.—The copper, as charged into the furnace, is brought to fusion as quickly as possible. If the material charged is cement copper, containing considerable impurities, a little air may be allowed to enter during the melting; if the copper is electrolytically deposited, it is advisable to reduce the amount of air so admitted to a minimum. The melting will usually take from 6 to 7 hours.

When the copper is melted, air may be freely admitted, and the molten copper is vigorously worked with copper rabbles to agitate the surface of the copper and facilitate the scorification process. This practice, in recent years, has been superseded by inserting a pipe into the molten metal by which compressed air at about 90 lb. pressure, is driven into it, agitating and at the same time oxidizing it. This is continued until most of the oxidizable impurities are oxidized, and about 6 per cent. of the copper is converted into cuprous oxide, which is held in solution of the molten liquid. This exerts a strong scorification action on such impurites as can be slagged. The metal at this stage exhibits a characteristic fracture and is called "set" or "dry" copper. Carrying the oxidation further only results in needlessly slagging copper.

During the scorification action, zinc, lead arsenic and antimony are partly volatilized, and partly oxidized; sulphur escapes as sulphur dioxide; iron, nickel, part of the zinc, and a portion of the copper are oxidized and slagged off, the necessary silica for the slag being furnished from the furnace bed. The slag also takes up all other substances that come to the surface of the molten copper. Besides the action of the air, cuprous oxide, which is held in solution in the molten bath, gives up its

oxygen to the foreign elements in the copper. The slag is skimmed off from time to time, so as to give free access of air to the metal. Most of the sulphur is eliminated with comparative ease, although a large amount of sulphur dioxide gas remains dissolved in the liquid copper, which gradually is driven out as the copper is worked and being oxidized.

After several hours the formation of slag almost ceases, and the evolution of bubbles becomes noticeable, which is due to the action of the cuprous oxide on the small quantities of cuprous sulphide which may be in the copper, producing metallic copper and sulphur dioxide.

Samples of copper, taken with an iron ladle, in the early stages of the process, before much oxidation has taken place, show a convex surface, often with sproutings of copper on top, which is due to the escape of sulphur dioxide from the copper during solidification. As the operation advances, the formation of bubbles slackens, the samples become denser, and as they cool, crater-like elevations form on the surface, through which the sulphur dioxide breaks out. When the boiling of the molten copper is over, the copper still retains a small quantity of sulphur dioxide, which is only given off during poling. By the time the copper shows from 5 to 6 per cent. cuprous oxide the samples will show a decided concavity, with a single bubble at the apex of the depression. The "set" or "dry" copper has a dull fracture and is of poor quality for any commercial purpose.

Reducing Stage.—After the oxidizing stage, and when the copper contains about 6 per cent. cuprous oxide, the reaction is then changed to a reducing one, by means of hydrocarbon gases evolved from green poles thrust beneath the surface of the molten metal and the copper brought back to "pitch" or when it contains about 0.6 per cent. of cuprous oxide, and gives castings, the surface of which neither rises nor falls when setting in an open mould. The metal in this state develops the best mechanical properties under subsequent treatment.

By poling, the reducing gases from the wood reduce the cuprous oxide to the metallic state, while the molten metal, due to violent agitation, is at the same time exposed to oxidation. The complete removal of the sulphur dioxide is indicated by the smooth surface of the sample. After the expulsion of the sulphur dioxide, which takes place in from 2 to 3 hours, the reduction of the cuprous oxide is commenced. A sample now taken has a brick-red fracture and shows columnar structure, which changes to cubical as the oxidation proceeds; at a still further stage the brick-red color has a strong violet tinge.

After the expulsion of the sulphur dioxide, the poling is still continued for 2 or 3 hours, while the surface of the molten copper is covered with charcoal to prevent reoxidation. As the reduction proceeds, the copper becomes softer and tougher. Samples are taken continually; they are dipped out with a small iron spoon, cooled in water, fastened in a vise

and broken. The cubical structure of the fracture gradually passes successively into a coarse columnar, a fine columnar, coarsely fibrous, and lastly into a finely fibrous structure. The color at the same time changing from violet to brick-red, yellowish-red, and lastly to a fine salmon pink. The copper becomes dense, and so soft as only to be broken with difficulty in a vise. The samples taken also show less concavity, as the operation progresses, until the metal has reached the condition of "pitch" when the surface remains flat.

The copper is now ready to be cast. In a small plant it is ladled out by hand, but in large works ladles holding 200 lb. of copper are used, each carried by an overhead trolley, and by which the copper is readily handled. The moulds are of different forms, or shapes called for by the trade; forming cakes for rolling into sheets, ingots for melting into brass, and wire bars for making wire. The copper still contains about 0.6 per cent. cuprous oxide.

Under-poled copper simply contains an excess of cuprous oxide as an impurity and suffers both in electrical and mechanical properties. Over-poled copper looks like under-poled copper under the microscope. The mechanical properties are satisfactory, but there is a slight decrease in conductivity and castings are bad, due to the expulsion of gases as the metal sets. Over-poled molten copper is, however, in a very unstable condition, and it is usual in such cases to start at the beginning of the refining operation and oxidize the metal again to set copper. The fact that molten copper is so sensitive chemically to its surroundings and that it chills so readily, is due to its high thermal conductivity and makes it a difficult metal to handle.

It takes very little to throw copper out of pitch, and any change is immediately shown by the appearance of the ingots. If, on cooling, the ingots contract, leaving a depression in the center, it indicates that suboxide is forming, and ladling must be stopped and the charge poled a little. Short sticks of green wood thrown on top of the copper assist in the reduction. If, on the other hand, the surface of the ingot rises and becomes convex, then the charcoal must be pushed back from the ladling door and the charge flapped or rabbled. It takes only a few moments to bring the copper back to pitch, and it is here that skilled labor is indespensable.

Ladling should be done as rapidly as possible, so as not to give the copper time to change its pitch. The fire should be previously attended to and everything arranged so that during ladling there will be an equally balanced oscillation between oxidizing and reducing action in the furnace.

The moulds are made of copper and are arranged on a shaft fastened to a bosh containing water, so that upon being tipped upside down the ingot falls out and drops into the water. This is done to give the ingot

a red-copper color due to thin coating of suboxide. Copper cast in iron moulds becomes porous.

The copper moulds are covered with a bone-ash washing before the molten copper is poured into them.

Although there is no relation between the color of the cast copper and its chemical composition or physical properties, nevertheless some attention is given to its external appearance. Castings left to cool in the air become coated with undesirable scales of oxides of a very dark appearance, which sooner or later become detached. To avoid this the castings are dropped into water. To obtain the most desired color, which is a lustrous one between that of gold and copper, the cooling bath is composed of hot water containing about 0.1 per cent. sulphuric acid. A rose pink color may be obtained by mixing wood tar with the water into which the copper is thrown after it has set in the moulds.

Furnaces Used for Copper Refining.—Reverberatory furnaces are universally used for copper refining. The furnace used for this purpose should be strongly built and thoroughly bound together. The entire bottom and sides should be encased in a cast-iron box.

Figures 71 and 72 show a modern furnace, designed by H. L. Bridgman, in which the sides and bottom are encased in iron plates. Below the skimming door, which is at the chimney end, there is a heavy cast-iron plate.

The hearth of a refining furnace is usually made of clear sand, carefully smelted in and saturated with copper to make a "bottom." The bed of small furnaces is usually fused in one layer, and in the larger furnaces sometimes two. The bed absorbs considerable copper, and it is best to saturate it with copper as far as possible before the furnace is actually put in operation.

In order to put in a new hearth, the furnace is thoroughly heated. Clean sharp sand is then put in and thoroughly heated till the water is driven off and all organic matter burned out. It is then brought to the shape required with tools made for the purpose, and beaten down. The doors of the furnace are then closed and a sharp fire kept up for about 12 hours, the temperature being raised to the highest point of which the furnace is capable. By this time the sand will be glazed; the doors are then opened and the furnace allowed to cool for 2 hours. From 1000 to 2000 lb. of scrap copper are then added, which melts and mixes with the sand at a very high temperature, and the furnace is then allowed to cool. Whatever copper does not sink into the hearth is ladled out as quickly as possible, and the operation repeated two or three times, if necessary, until the bed is from 10 to 15 in. thick. When the last addition of copper is melted, the hearth is cooled for 2 hours, and the furnace is then ready for use.

The copper is charged through working doors at the side of the

furnace, although quite frequently provision is made to charge through a hole in the arch. The refined copper cannot be tapped out, because of its extreme tendency to chill and clog the tap hole. Ladles are therefore used to cast the copper into moulds. The bed of the furnace

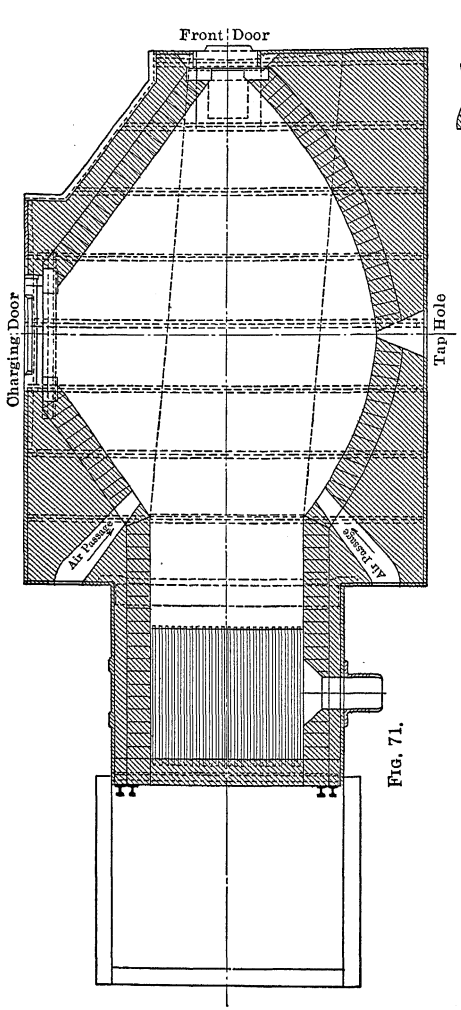


Fig. 71.

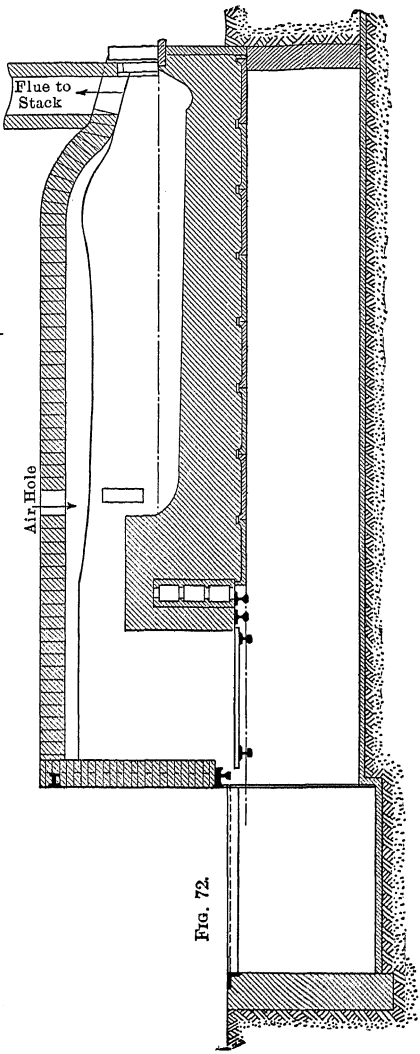


Fig. 72.

Figs. 71 and 72.—Copper refining furnace. Bridgman's design. Plan and longitudinal section.

slopes from all sides toward the ladling door, at which there is a depression to act as a well. The ladling door, which may also be used as a working door, is located at the flue wall, so that the cold air entering may pass directly into the stack, without either cooling or oxidizing the molten copper.

Wood is the best fuel to use because it does not contain any sulphur

or other impurities to affect the copper injuriously. Next to wood, bituminous coal presents the most advantages; coal containing sulphur should not be used. The coal should be fired with a smokeless flame.

The size of furnaces varies exceedingly; from 1 to 2 tons at a charge as used in the Siberian refineries, to 15 and 20 tons as now used at Lake Superior.

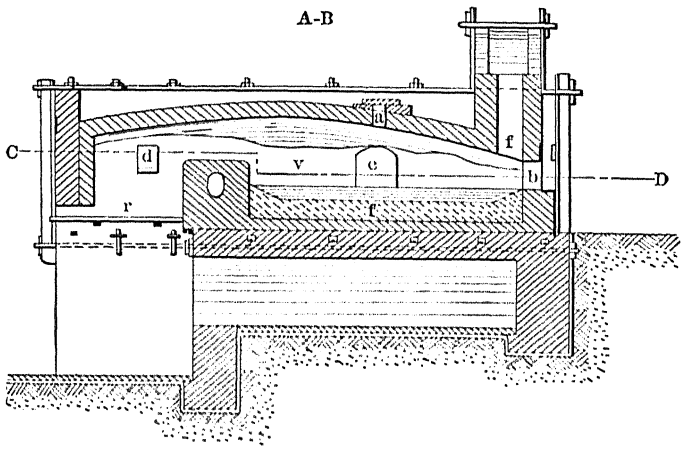


FIG. 73.

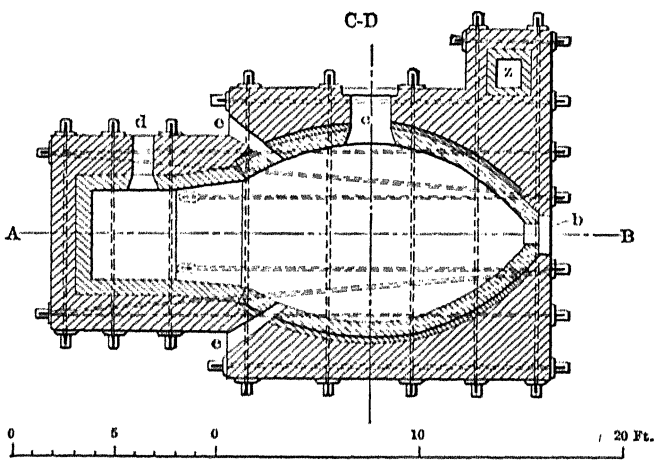


FIG. 74.

FIGS. 73 and 74.—Mansfield copper refining furnace. Plan and longitudinal section.

At Lake Superior the weight of coal required for refining is about 50 per cent. of the weight of the copper refined.

Figures 73 and 74[1] show the refining furnaces used at Mansfeld. The charge consists of pulverulent cupric oxide with some ferric oxide,

[1] Schnabel, Handbook of Metallurgy, Vol. I., p. 183.

which is charged with a sufficient proportion of charcoal for its reduction, the charge being 5 to 7 1/2 tons. This is reduced in the first part of the process and then immediately refined.

In the figures *v* represents the body of the furnace, *a* the aperture in the roof for charging, *f* the bed made of quartz to which a little slag has been added, *r* the grate worked with a clinker bed, *d* the fire door, *f* the flue, *c* a door for charging the big lumps if required, *b* the working door through which the copper is also ladled out. At *e e* there are two channels for the admission of air to the furnace, this being regulated by more or less blocking the channels with bricks.

Copper Refining at Kedabey, Russia.[1]—Fig. 75 gives the form and arrangement of the refining furnaces at Kedabeg, Russia, of a minimum capacity of 7.2 tons in 24 hours, or of four charges of 2600 to 5400 lb.

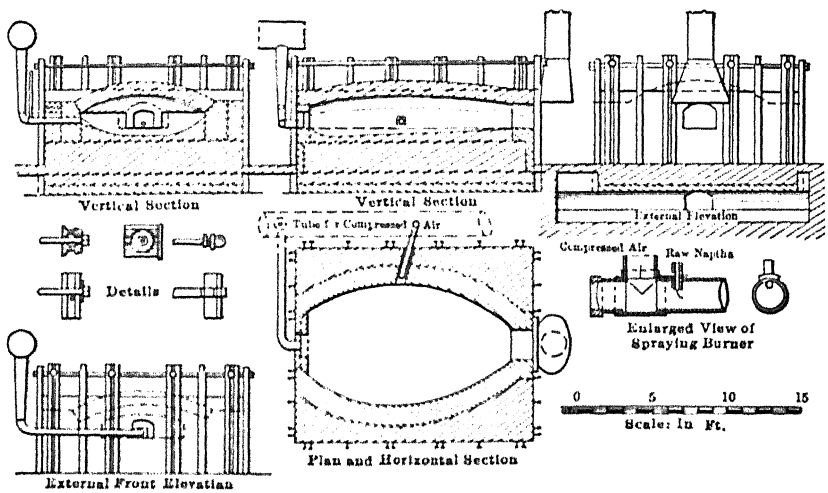


FIG. 75.—Kedabeg oil fired copper refining furnace.

of black copper. The furnaces are fired with oil; the oil jet is sprayed into the furnace at the middle of the long sides, and is met in addition by an air blast at the working door end, which serves to complete the combustion of the gasified petroleum. The flame thus sweeps over the hearth and escapes by means of a short stack of sheet iron.

The time of melting down is performed in 2 to 2.5 hours, with the blast at low pressure, which effects a complete combustion of the oil and partially oxidizes the impurities. The blast is then turned on the molten bath, and the full pressure of 1 in. of mercury through a tuyère directed downward upon the surface of the metal. Sulphur, arsenic, and antimony are volatilized, much smoke being given off. The zinc and iron begin to slag off together with some copper oxide. The slag

[1] Trans. Inst. and Metal., Apr. 13, 1905.

is skimmed off as it forms. This operations lasts from 1 to 1.5 hours, after which the rabbling or roasting begins.

The roasting is characterized by the escape of bubbles of sulphur dioxide at the surface of the molten copper due to the well-known reactions between the oxides just formed and sulphide of copper, of the black copper. This takes 2 to 3 hours.

When the surface of the molten bath has become perfectly quiescent, the poling begins, which is continued until a sample withdrawn with a spoon, shows the characteristic cubic structure, quite free from blow holes, after which the final reduction of the copper is proceeded with, poling being completed under a cover of coal dust until the copper reaches the desired strength and toughness, characterized by a rose colored fracture and silky structure, and by standing hammering and bending without cracking, both hot and cold.

The amount of oil equals 75 per cent. by weight of the copper produced. For two furnaces there are needed per shift, one foreman, one furnaceman, and four helpers, these latter for charging and tapping.

At Kedabeg[1] small furnaces were also used for refining supplied with blast, wood being used as the fuel. The charge was 2880 to 3240 lb. of coarse copper, and the time occupied 8 hours, three charges being worked in 24 hours. Of the time occupied for one charge, 1/2 hour was consumed in fettling and charging the furnace, 2 1/2 hours in fusion, 3 1/2 hours in scorification and boiling and 1 1/2 hours in poling. The fuel used in 24 hours was 1 1/4 cubic fathoms of wood. Each 3600 lb. of coarse copper yielded 2952 lb. of refined copper of 99.68 Cu, and 900 lb. of refinery slag containing 30 to 59 per cent. copper.

[1] Schnabel, Handbook of Metallurgy, Vol. I, p. 195.

CHAPTER XVIII

COPPER SULPHATE; BLUESTONE

Copper sulphate is an important article of commerce, and great quantities are annually used in the various arts. It is largely produced as a by-product in the electrolytic refining of copper in the purification of the sulphate solutions. It is also largely produced from the metal by working up the cement copper to recover the gold and silver. It may be produced direct from the ore and from copper matte.

For districts where iron is expensive, it has frequently been proposed to leach the ore with sulphuric acid to saturation with copper sulphate, and then by evaporation crystallize out the copper sulphate and market the copper in that form, rather than to attempt to get the copper in the metallic condition.

The composition of crystallized copper sulphate is $CuSO_4,5H_2O$; therefore, only 25.1 per cent. of the sulphate is copper, and the rest is sulphuric acid and water. The only valuable constituent of copper sulphate is the combined copper and forms the basis of the price of copper sulphate. The combined acid has no special value and the water is valueless. In the manufacture of copper sulphate direct from the ore, a product has to be freighted and marketed, only 25.1 per cent. of which has any real value. It therefore follows that the conditions which would prohibit the importation of iron for the precipitation of the copper would also prohibit the exportation of the copper sulphate. Moreover, the sulphuric acid, combined with the copper as sulphate, might by a regenerative method, be turned into profitable account in leaching fresh quantities of ore.

Copper sulphate is largely produced as a by-product in the process of refining silver and gold bullion with sulphuric acid. The silver and gold alloy is boiled with concentrated sulphuric acid in cast-iron pans; the silver is dissolved and goes into solution with the copper, while the gold remains as a mud, which is collected and melted into bars. The silver sulphate in the solution is then precipitated by metallic copper, and melted into silver bars. The copper sulphate is then crystallized out of the solution, thus recovering in a marketable form the original copper of the material treated.

Copper sulphide ores, chalcopyrite, and chalcocite, and copper matte, are sometimes converted into blue vitriol.

If the roasted copper ore or matte is treated with dilute sulphuric

acid the solution obtained will have, in addition to cupric sulphate, salts of iron, arsenic, antimony, bismuth, cobalt, nickel, etc. A solution of this character cannot be used direct for the manufacture of blue vitriol, because these salts to a certain extent will crystallize with the copper sulphate, and make it too impure for the market. If the crystallization is made from an impure solution, and the crystals of copper sulphate are contaminated with ferrous sulphate, the iron may be removed by roasting the salt until the ferrous sulphate is decomposed into oxide, and then dissolving in water and recrystallizing. It will usually be found better to treat the impure solution with some oxidizing agent to convert the iron to the ferric state, when, by adding copper carbonate, or oxide, or barium carbonate, and boiling again, the iron is precipitated.

At Freiberg, Saxony[1] copper sulphate is made from matte which has been repeatedly roasted and smelted to eliminate most of the impurities. The original matte contains about 40 per cent. copper, and this is concentrated to a richer and purer product containing about 70 per cent. copper and only 0.3 per cent. iron. This matte is crushed to pass through a 1/4-in. mesh screen and roasted 12 hours in a reverberatory furnace. The charge of 1000 lb. is continuously rabbled and thoroughly roasted.

The roasted matte is screened and treated with dilute sulphuric acid in upright cylinders, 2 ft. 8 in. in diameter and 3 1/2 ft. high, made of 1/2-in. lead supported by an iron framework, which is covered with thin sheet lead. The cylinder has two outlets, one at the bottom for discharging the residues, and the other higher up for withdrawing the copper solution. Steam is injected through a lead pipe near the bottom of the cylinder. This pipe is so arranged that it can be raised or lowered.

The cylinder is charged with 3 cu. ft. of mother liquor, and 3 cu. ft. of common sulphuric acid of 45 to 47° B., which gives a solution of 34 to 36° B. Superheated steam is then applied, and when the solution is boiling, 200 lb. of roasted matte is gradually charged with a hand shovel through a movable funnel. The matte has to be fed continuously. After a quarter of an hour, 9 cu. ft. of mother liquor is added to the contents of the cylinder, which fills it to about 7 in. below the rim. The boiling with steam is continued for 4 or 5 hours, during which time stirring has to be done at intervals. The steam is turned off, and half an hour is given for the residues to settle. Then the solution is drawn off through the upper outlet and conveyed to settling tanks, while the residue, containing all the silver and about 5 per cent. copper, is transferred into a special basin, where it is washed with water. The still hot copper solution is left about an hour in the settling tanks, during which time some basic iron salts settle. Then it is drawn off into crystallizing tanks. The residues are dried and transferred to the lead smelter.

The blue vitriol crystals after 5 to 7 days are removed from the

[1] O. Hofmann, "Hydrometallurgy of Silver" P 258.

crystallizing tanks. They are not of a clear blue color, but have a greenish appearance from a certain percentage of iron which they contain, and are again dissolved and recrystallized. All the solutions are very acid. The yearly production of blue vitriol resulting from this process is about 800 tons.

The Oker Process.—The usual method employed by bluestone manufacturers is to make use of the crude metallic copper, containing the precious metals; granulate it, and alternately subject it to the action of air and warm dilute sulphuric acid. The copper is oxidized by the air and dissolved by the acid, and yields a copper sulphate solution which is crystallized into a reasonably pure product, and mud residues, which contain the silver and gold and other impurities.

This method originated and is still in operation at Oker, Germany, for which reason it is called the Oker process.

The granulated copper is charged into lead-lined wooden tanks, 5 ft. high and having a bottom diameter of 3 1/2 ft. and a top diameter of 2 1/2 ft. About 5 in. from the bottom is a movable wooden filter made by perforating the boards with inch holes. At the side of the tank, between the bottom and the filter, is cut an opening 4 in. deep and 8 in. wide which serves as an outlet for the solution and inlet for the air. To this opening is attached a lead trough. In charging the tank, large pieces of copper are first placed on the filter bottom, and then the granulated copper, amounting to about a ton, is charged on top of the coarse pieces. A spray of dilute sulphuric acid of 28° B., and heated to 70° C., is then applied to the copper granules in the tank. The first solution, issuing from the tank, shows no color and contains but little copper sulphate. The spray is applied intermittently. By the evaporation of the warm solution and condensation of the steam a gentle draft is produced through the charge and the oxidation of the copper takes place with the formation of cupric sulphate. After a quarter of an hour more hot acid is applied, and the stream of acid dissolves the cupric sulphate formed, leaving the surface of the granules clean. The air again entering the tank, oxidizes more copper, which is again washed out by the acid, and this process is repeated indefinitely. Instead of pure acid, crude copper solution, or acid mother liquor, is mixed with the acid to dilute it, instead of water, which has a more energetic dissolving action on the copper. The strength of such a solution is regulated at 32 to 34° B.

Silver, gold, arsenic, antimony, lead, and other impurities remain as slimy residues and are washed out with every charge of acid, and settle in a horizontal trough 160 ft. long, 30 in. wide and 14 in. deep. The solution in this horizontal trough moves slowly, and when it reaches the outlet has cooled to a temperature near that of the surrounding air. The crystals of blue vitriol which form in the trough are shoveled out on an inclined bench which lets the adhering solution drop back into the trough.

This is done every 3 days. The mother liquor flows into a pressure tank and is lifted to a reservoir placed on a floor above the dissolving tanks. This liquor contains much acid, and after mixing it with still more acid it is heated and used for dissolving the granulated copper.

The crude bluestone which was shoveled out from the trough and to which some slimes are adhering, are first washed with a spray of water, then dissolved in a lead pan by boiling with water or with a mixture of water and mother liquor from the second crystallization. Crude vitriol is added until the solution measures 29° B., after which the fire is stopped and the sediment allowed to settle. When the solution has somewhat cooled and become clear, it is very carefully decanted, and conveyed to wooden lead-lined crystallizing tanks 147 cu. ft. capacity. Ten days are allowed for crystallization.

Clemmer gives in detail a description of a commercial plant producing blue vitriol from metallic copper.[1] He prefers the granulated copper which contains silver and gold. No particular care is required to free the copper from impurities other than iron, and the granulation of the copper is quickly and cheaply accomplished by providing a walled and cemented well at the tapping side of the furnace. The well must have a continuous flow of water during the time of granulation. The dimensions of the well will depend upon the capacity of the furnace or the charge of copper used, and must be large enough to keep the granulated copper submerged in the water while tapping. An iron bucket handled by an overhead stationary or travelling crane, fits loosely in the well, and receives the granules. An iron spout from the tap hole of the furnace projects over the side of the well, and during the tapping a pole of green wood is held under the stream of molten copper, which granulates it sufficiently for the purpose. While the copper is flowing from the furnace care must be taken to keep the stream thin, and to have an intermittent flow, otherwise explosions will take place.

The cheapest grades of copper mattes from lead works are the most economical for this purpose. These contain silver and gold, and furnish an additional source of profit, as the precious metals are recovered as a by-product in the form of rich slimes, assaying 7000 to 10,000 oz. silver per ton. The following analyses are of copper mattes of this character:

Source	Cu %	Ag %	Fe %	As %	Sb %	Pb %	Zn %	Si %	S %
Pennsylvania Lead Co.	43.40	0.34	14.36	1.04	0.63	13.04	1.39	0.27	24.96
St. Louis Smelt. & Ref. Co.	42.01	0.47	14.00	0.39	0.07	16.30	2.49	0.20	23.85
Kansas City Smelt. & Ref. Co.	40.10	0.38	15.44	0.56		17.37	1.89	0.30	23.40

[1] Min. Ind. Vol. IX, 278.

The dissolving of the granulated copper with sulphuric acid without a previous furnace oxidation is accomplished by placing the granules in short towers (called "oxidizers" and "dissolvers") 3 ft. long, 3 ft. 3 in. wide and 6 ft. 6 in. deep, inside dimensions, and lined with lead of 15 lb. per square foot.

Each tower has an opening 1 ft. square at the bottom and center of the front, which serves as an outlet for the liquors and an inlet for air. The towers are provided with false bottoms to support the granulated copper, made of several 0.75-in. iron pipes, each covered with a heavy lead pipe with the overlapping ends closed. These pipes are placed side by side 3 ft. from the bottom, upon chemical bricks set in the towers to the right and left of the bottom openings. The air space under the false bottom serves to collect the silver slimes.

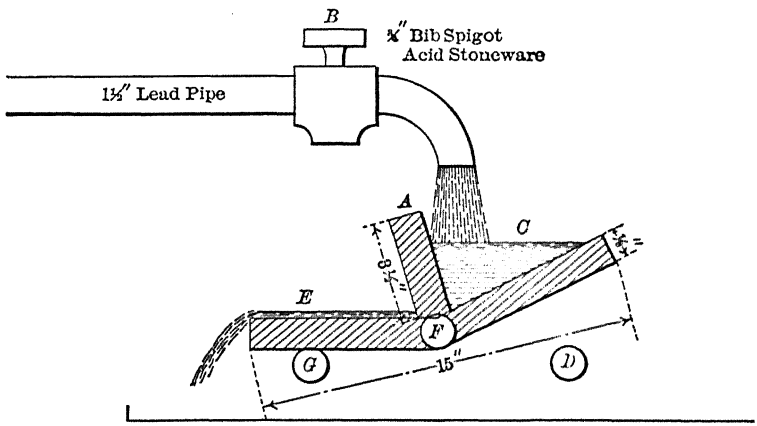


FIG. 76.—Oscillating trough for distribution of acid.

The proper condition of the sulphuric acid for the most rapid solution of the copper is 10° B. strength at 190° F. temperature. The acid is spread over the granulated copper in each tower through a flanged sheet of lead perforated with two quarter-inch holes for each square inch of surface. These sheets are placed upon the top of the shot copper and the spreading of the acid is accomplished by an oscillating trough. The trough, 34 in. long, is divided longitudinally by a partition, *A*, Fig. 76, and the lead pipe and cock, *B*, convey the acid from a reservoir into the top compartment, *C*. When this is full, the trough turns on its axis, *F* (its center of gravity being changed), until it is stopped by the rod, *D*, and the acid flows out. As a result of this turning, the second compartment, *E*, is elevated, and when filled in its turn is tilted back to its first position, where it is stopped by the rod, *G*. In this manner the continuous oscillation of the trough distributes the flow of acid, first to one side and then to the other. The troughs are made of 0.875 or 1 in. wood, prefer-

ably yellow pine. The ends, bottom and partition are grooved and pinned together, the axis being an extended part 3 in. long, from each end of the bottom. When put together it is soaked in thin turpentine asphaltum to increase its durability. The trough may consist of a lead covered iron frame, but this is more expensive to construct.

The strength of copper sulphate liquor issuing from the towers will naturally depend upon the speed and heat of the acid delivered into them and must be regulated according to requirements. The towers, or dissolvers, are daily replenished with copper, added by a shovel, after removing the perforated lead sheets. During this charging it is not necessary to shut off the flow of acid. It is a good plan to shut off the acid supply to one tower at a time, at intervals of about a month, and wash out the towers with water under pressure, removing the wash water and residues to the slimes tank by a movable spout. This operation separates the slimes adhering to the shot copper, and allows their quick conversion into a marketable condition, and, in addition, it aids the acid attack on the copper.

The slimes which collect in the free space at the bottom of the tower may be removed at any time without washing out with water or shutting off the acid.

For a small plant producing 5000 lb. of copper sulphate per diem, six dissolvers, as above described, will be ample; with these should be connected 10 crystallizing tanks, $10 \times 10 \times 3$ ft. deep, inside dimensions. It is preferable to taper the crystallizing tanks each side 1 in. from top to bottom for the better adherence of the crystals. This construction modifies the dimensions to 10×10 ft. at the top and 9 ft. 10 in. $\times$ 9 ft. 10 in. at the bottom. The crystals form on lead straps, hung in the tanks from wooden cross-pieces, and completely surround them, and cannot fall off. When the sides of the tank are perpendicular, the lead invariably "buckles" from the hot liquor and the weight of the attached crystals. This objection is overcome with the inclined sides, as each crystal naturally supports the upper ones next adjacent to it, and as a result the entire mass of crystals on the sides is of greater strength and durability. Each tank is emptied of the mother liquor at the end of the crystallizing process by means of a plug and plug seat; the latter is burnt to a lead pipe, which leads to a trough or gutter, generally a tank set below the level. This method requires much less time than the customary siphoning operation, which has the additional disadvantage of leaving a layer of liquor at least 1 in. high that must be dipped or shoveled off.

An alloy of 90 per cent. lead and 10 per cent. antimony gives excellent results when used for making the seats and plugs.

The plant is generally arranged in terraces so that the transportation of the liquors will be accomplished by gravity. The acid tanks are at the highest level with the towers, directly in front on the second level;

the combined receiving and settling tanks are placed on the third, and the crystallizing tanks on the fourth and lowest level. The gravity floor is completed at the mother liquor tank, which is sunk in the earth below the last level. The crystallizing tanks are arranged in double rows, with a 2-ft. space between, and are constructed on the lead covered floor placed directly on the earth surface, which is inclined toward the sump and serves as a common receiver for the entire system. The space between the double rows slopes to a gutter for the convenience of the mother liquor and any leakage to the sump. The wash floor for the crystals is in front of the crystallizing tanks, and slopes toward the sump for the collection of the wash waters. A continuous drying apparatus is placed on the other side of the floor, opposite the tanks.

This arrangement furnishes a gravity flow of the liquors from the acid tanks at the topmost level, through the towers, receivers and settlers, crystallizers and finally to the sump. The acid, of course, must first be raised to the acid tanks, generally done by a steam injector.

When the plant is not terraced, but constructed on the level, the cost of handling the liquors by steam injectors from tank to tank is considerable.

The weights of the sheet lead for lining the tanks, expressed in pounds per square foot of surface, gave the best results when selected as follows: Acid reservoirs, 10 lb.; towers, 15 lb; receiving and settling tanks, 8 lb.; crystallizing tank, bottom, 10 lb.; sides, 8 lb.; floor under tanks, 3 lb.; gutters, 6 lb.; wash floors, 10 lb.; sides, 8 lb.; and sump tank, 6 lb.

The proper strength of the sulphuric acid to start the process of dissolving the shot copper is 10° B. By the passage of this acid several times through the dissolvers, or towers, in the manner described, it is concentrated to crystallizing strength, which for the best results, is 34 to 35° B. at 60° F. The crystallizing liquor should contain not more than 1 per cent. of free sulphuric acid, as this small quantity does not affect the appearance or quality of the crystal, nor does it in any way injure the sale; in fact, it adds weight, which is not copper, to the crystal, and costs less than copper—an item not to be overlooked.

Should the solution or liquor from silver-bearing copper be made neutral, in the dissolving towers, all the impurities will be precipitated in the silver slimes. This neutral solution, however, dissolves silver, and loss will ensue unless sodium chloride, or preferably hydrochloric acid, is added, to precipitate the dissolved silver as chloride, and to collect it in the slimes. Best results are therefore obtained by leaving 1 per cent. free acid in the liquor ready for crystallization. At the completion of the crystallizing process, during which the liquor has had ample time to segregate, those sulphates of lesser specific gravity than copper sulphate will have risen to the top, and may be drawn off from the copper mother liquor; their small amount of copper is regained by

pouring the solution over scrap iron, which precipitates it. In this manner the mother liquors, after dilution with water, can be used, in place of fresh acid, for the dissolving towers; and in actual practice there is very little danger of the liquors becoming too foul for crystallizing purposes. Electrolytic refiners who boil down their electrolytes for crystal, and run the remaining solution over scrap iron, may find it profitable to adopt the above practice; and in the electrolytic process itself this point may be of advantage, as it naturally follows that the electrolyte will segregate in the depositing tanks if its circulation be stopped for a few hours. The greater portion of the arsenic and impurities in the solution may be drawn off and removed to the bluestone department, thus avoiding excessive recrystallizing of the solutions. This method has been successfully used for some years with anodes made almost exclusively from foul, leady mattes.

With a standard strength of the liquor, the size of the crystal will depend upon the number of straps suspended in the tanks. In other words, the greater the surface for the blue vitriol to crystallize upon, the smaller the size of the crystal, and *vice versa;* slow cooling of the liquor favors the prevention of small crystals. In a few blue vitriol plants of ancient construction the crystallizing tanks were $8 \times 6 \times 6$ ft. deep to prevent the liquor from cooling too quickly. Tanks $10 \times 10 \times 2$ ft. deep also have been used; the best size, however, is $10 \times 10 \times 3$ ft. deep. In use, the tanks should be covered immediately after filling, with loose boards to prevent the "salting out" of the blue vitriol with the consequent formation of too great a quantity of "fines" and, of course, a lessened production of crystals, which, under these conditions, are small in size.

The crystals are dried quickly and cheaply by passing them through a revolving brass screen (0.25-in. mesh) enclosed in a small wooden chamber, with sides removable in sections. The chamber is heated by live or exhaust steam, and has a small exhaust fan to remove the moist air. The crystals are fed by copper conveyors into the screen, the exit end of which is sufficiently elevated to feed the dry crystals into a barrel. The "fines" which pass through the screen are carried by conveyors from below the screen to any part of the plant desired. The usual method of working the "fines" consists in placing them in a perforated lead basket suspended in heated and diluted mother liquors, and recrystallizing them from the solution thus formed.

The cost of manufacturing copper sulphate depends largely upon the capacity of the plant. Profit is sometimes made by producing the copper instead of purchasing it on the market, and a sulphuric acid manufacturer has an advantage of a supply of acid at first cost, and an outlet for his "weak distillates," which can be used for copper sulphate production, thus saving him the expense of reconcentrating them.

A favorable combination for diminished cost of production would be the combination of the process as above outlined, with the manufacture of sulphuric acid and metallic copper at a plant located near New York City; this location affording a saving in freight charges. Under these conditions it is estimated that the cost of making 5000 lb. copper sulphate, ready for shipment, per day, assuming the manufacturer also produces copper and sulphuric acid and that the location of plant is in the vicinity of New York City, would be about as follows: Copper and sulphuric acid, $152.63; foreman and labor, $11.50; packages, $4.80; fuel, $9.00; repairs, insurance, depreciation, etc., $6.00; total, $183.93, or about 3.73 cents per pound. This estimate may be considered high.

Hofmann's Copper Sulphate Process.[1]—Ottokar Hofmann's process is based on the reaction that, if through a hot neutral solution of cupric sulphate which contains ferrous sulphate a stream of air is forced, and at the same time cupric oxide is added, ferric oxide is precipitated and cupric sulphate will go into solution. Instead of specially prepared cupric oxide, roasted copper matte is used, which contains sufficient cupric oxide for the reaction.

The solubility of red oxide of iron in sulphuric acid increases with the strength of the acid, therefore it is not advisable to bring the matte in sudden contact with too strong acid. Cupric oxide dissolves so much easier than the iron oxide that a weak acid can be used which will readily dissolve the cupric oxide, but very little of the iron oxide, and the resulting cupric sulphate solution will be much purer. The strong first solution makes this method not suitable to be worked on a really large scale, because concentrated solutions require but little cooling to form fine crystals, which are very annoying in the separation of the residues from the solution, because these crystals will form in the filter-press, clog the filter cloth and prevent a free filtration. They will form in the mass of the residues, whence they can be removed only by a prolonged washing with hot water, causing the formation of too large quantities of very weak solution.

Hofmann modifies the manner in which the dissolving of the roasted matte is performed, inasmuch as the roasted matte is not added to the bulk of acid of sufficient strength to produce at once a cupric sulphate solution of the required concentration, but the solution is gradually enriched in copper until the desired degree is reached. This is done by preparing first a 3 per cent. acid solution. Such a weak acid dissolves but very little iron oxide. Then, when hot, the copper is added gradually as a stream of roasted matte, while at the same time a small stream of 60° B. acid flows into the tank. The solution in the tank is agitated vigorously by a machine stirrer. The proportion of matte and acid has to be so regulated that the solution always maintains its strength of 3

[1] Hofmann, "Hydrometallurgy of Silver," page 259: Min., Ind., Vols. VIII and X.

per cent. in acid, while the content of the copper increases. This is controlled by frequent volumetric tests. When the desired strength of copper is nearly attained, the influx of acid is stopped and only so much matte added as will neutralize the 3 per cent. acid. Thus the copper matte does not come in contact with a stronger acid, and the resulting solution does not contain more than 0.7 to 1 per cent. iron, notwithstanding that the treated material is very rich in iron oxide.

The process was introduced by Hofmann in the large smelting works of the Consolidated Kansas City Smelting and Refining Company, at Argentine, Kansas, for the treatment of the argentiferous leady copper matte, first on a medium scale, but on account of its successful working it underwent an enlargement every year until a daily capacity of 60 tons of blue vitriol was reached. The plant is not now in operation, the smelting works with which it was connected having been closed down and dismantled in 1902.

The material treated is a leady copper matte containing 34 to 40 per cent. copper and 12 to 14 per cent. lead. It is crushed first in a rock breaker and then pulverized in a Krupp ball-mill of 100 tons daily capacity through a screen of 50 meshes to the lineal inch. The roasting is done in three two-story Pearce turret furnaces, each provided with three fire places at the lower and two at the upper hearth. For the benefit of the subsequent operation the roasting has to be conducted with great care, and with attention equally divided between the oxidation of the copper and of the iron. The copper is to be converted into the cupric oxide and sulphate, and the iron into red oxide, in which state it dissolves only slowly in hot dilute sulphuric acid. The formation of cupric sulphate is very desirable, as it saves acid in the subsequent treatment, but still it is not advisable to conduct the roasting so that as much as possible sulphate is formed, because the roasted material will then contain too much soluble iron, which would make the resulting cupric sulphate solution too impure. At a comparatively early stage of the roasting nearly all the copper is in a state in which it can be extracted by dilute sulphuric acid; about 75 per cent. of it is present as oxide and 25 per cent. as sulphate. The roasting, however, cannot be considered complete at this stage, because the roasted material still contains too much soluble iron.

At the beginning of the operation the temperature should not be raised above that produced by the combustion of the sulphur of the matte. During this period the charge assumes a rather bright red appearance, an effect due more to light than to heat, and if excess of air is admitted to the furnace but few lumps will form, even with very leady copper matte. Gradually, as the oxidation advances, the surface of the charge becomes darker, especially near the ore doors, and when the entire surface of the charge begins to darken, the fire is slightly increased

to prevent cooling, as from this time on the supply of heat furnished by the oxidation decreases rapidly. If this condition is overlooked and the charge cools too much, it will be difficult to raise the temperature again to the proper degree.

The roasting is continued at a moderate temperature until no more heat is evolved by the oxidation of the material, after which the temperature must be raised to a cherry red. A skilled roasterman can readily determine this point by stirring the charge; if the particles thrown to the surface brighten, the roasting has not advanced far enough, but if the entire charge presents a dead and uniform red color, it shows that this part of the roasting has been completed, and that it is time for an increase in temperature. This can now be done without danger of lumping the charge, because by this time the greater part of the sulphides has been oxidized.

The increase of the temperature is necessary for two reasons: first, to hasten the oxidation of the remaining sulphides, which would require a very long time at a low temperature, and second, in order to decompose the iron salts and to convert them into the red oxide. The task for the roasterman is to convert as much as possible into the red oxide without decomposing the cupric sulphate present. Cupric sulphate resists considerable heat, more so than the ferrous salts, and it is possible to conduct the roasting in this way; but the increase of temperature requires judicious care, because if the heat is too high the cupric sulphate will be reduced to cuprous oxide, in which condition but half of the copper is soluble in diluted sulphuric acid. If crystals of cupric sulphate are exposed to heat and air, it will be noticed that after the acid has been expelled the mass assumes a red color showing the formation of cuprous oxide. If heating is continued, it turns black by being oxidized to cupric oxide. Should cuprous oxide be formed, the amount of extractable copper will be greatly reduced. When the roasting is done in a common reverberatory furnace, a mistake of this kind can be corrected by keeping the charge longer in the furnace and thus oxidizing the cuprous to cupric oxide. In a mechanical continuously discharging furnace, however, this cannot be done, but with experience and care the decomposition of the cupric sulphate can be avoided. It is of great importance that, during the whole of the roasting, air has free access into the furnace.

It is not possible to avoid the formation of lumps, especially in roasting leady matte, but if the roasting is conducted properly, these will be small, soft, porous, and consist of well roasted material. Roasted matte is always of coarser grain than the raw pulp, and for this reason as well as on account of the lumps it is necessary to pulverize the roasted material before treatment with sulphuric acid. This is best done in a Krupp ball-mill through a screen with 50 meshes to the lineal inch.

The dissolving at Argentine, Kansas, is done in eight agitating or stir

tanks, which are arranged in two parallel rows with a track between for the delivery of the matte. The cars are scoop-shaped and are partly covered with sheet iron, and so made that the cover and scoop end come close together, leaving only a narrow slit open, so that when the car is

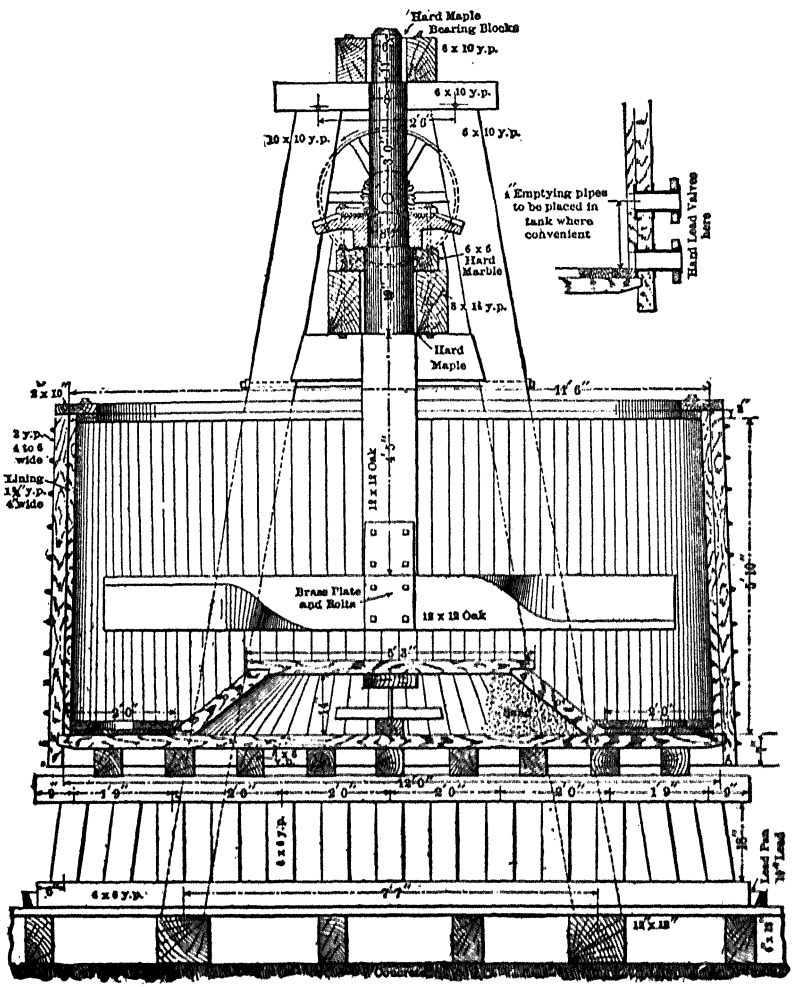


FIG. 77.—Stir tank, vertical section.

tilted the roasted matte runs gradually in the dissolving stir tank. Fig. 77 represents the vertical section of a stir tank, 12 ft. in diameter and 6 ft. deep. The bottom and sides are lined with boards for protection against wear from the friction of the pulp. In the center is suspended a heavy wooden shaft, having fastened to the lower end, by heavy brass plates, a cross-beam cut at both ends like a propeller-blade. In the

center, below the propeller and fastened to the bottom of the tank, is a cone-shaped projection constructed of strong wooden staves, the interior of which is filled with sand. This cone forces the matte, when the propeller is in operation, toward the periphery, where it is subjected to the swift rotating motion of the liquor, thus preventing its accumulation in the central part, where the motion is much less. Two outlet pipes provided with hard-lead valves make connection with the pressure tank. These are placed one above the other to permit the withdrawal of a portion of the clear liquid if desired, in which case the paddle is stopped and the residues allowed to settle. In the usual working of the tank, however, the lower outlet only is used. The wooden ring attached to the rim of the tank prevents the splashing of the pulp. The tank and trestle support are placed in a flat lead pan to collect any leakage. The upper part of the shaft is provided with a gear-wheel to receive the power.

The stir tanks are filled about two-thirds full with water, the agitator set in motion, and sulphuric acid added until the liquid shows about 3 per cent. acid. The matte is then charged gradually, and at the same time a stream of acid is allowed to flow in so as to maintain the same acid strength during charging. In this way the dissolving is accomplished with an acid strength of 3 per cent. or less, and still yields a strong solution of cupric sulphate. As stated above, it is preferable to work with weak acid, because much less iron and other impurities will be dissolved than with stronger acid. When the solution has attained a strength of about 20 to 22° B., the flow of sulphuric acid is stopped and matte only charged until the solution is neutral. Toward the end it is advisable to charge the matte at intervals, and to make frequent acid tests to avoid an excess of matte. The addition of sulphuric acid to the water, and the matte to the diluted acid, produces heat, which aids the solution of the cupric oxide. This heat is not sufficient, and the temperature is further raised by a jet of steam. It is well to interrupt the charging of the matte while neutralizing as soon as the solution shows 1 per cent. free acid. If the agitation is then continued this 1 per cent. of acid will be diminished, but if in half an hour after the acid test the percentage of free acid remains the same, more matte is added until the solution is neutral; in this way a mistake of adding a large excess of matte is avoided.

Below the stir tanks are the pressure tanks, into which the finished charge is drawn while the paddle is in motion. On account of the residues the pressure tanks are in an upright position, and are constructed as follows: the body consists of two cylindrical sections 4 ft. long and 4 ft. 6 in. in diameter, the bottom being of a spherical shape of 2 ft. 3 in. radius. The top is rounding upward to a height of 6 in. above the rim. The sections are tightly flanged, with a rubber gasket between. Four pipe connections are made through the top; the discharge pipe entering

through the center passes nearly to the bottom, and the filling pipe, air-inlet and air-outlet pipes are conveniently arranged around it. By proper connection with the filling pipe and by the use of valves, one pressure tank is made to serve four stir tanks. The upper cylindrical section is provided with a manhole, and the tanks are made of cast iron and lined first with lead and then with wood to protect the lead from wear by abrasion. The air pressure required is from 40 to 50 lb. Fig. 78 shows the top view and Fig. 79 a vertical section of an upright pressure

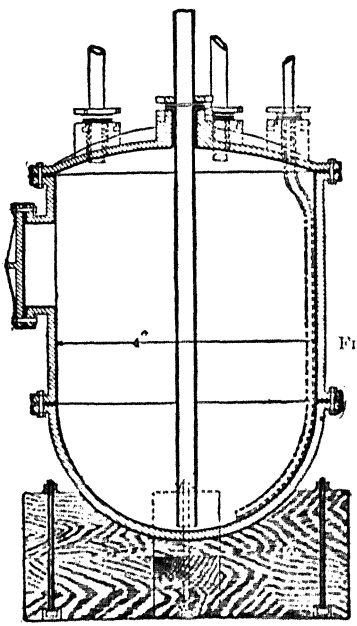


Fig. 79.

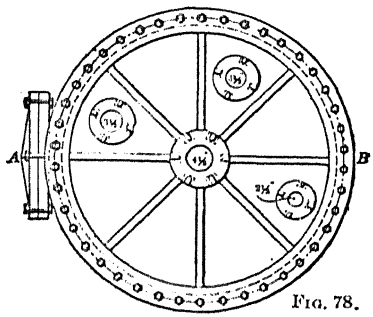


Fig. 78.

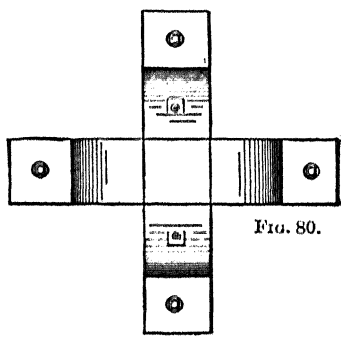


Fig. 80.

Figs. 78, 79, 80.—Cast iron pressure tank. Fig. 78 (top right), top view; Fig. 79, section on line AB; Fig. 80, plan of supporting frame.

tank, while Fig. 80 illustrates the supporting frame. This tank as represented by the figures is smaller than those used at Argentine, and has only one cylindrical section instead of two. The general arrangement, however, is the same. The air inlet extends downward along the side, ending near the discharge pipe, in order to keep the residues near the outlet in a loose condition and prevent the pipe from clogging. For this reason it is advisable to have a small stream of air enter during filling.

The pulp is forced by the pressure tank into a large filter-press, of which there are five in use. The press is 25 ft. long and has hardwood frames and plates, and holds, when filled, 5 tons of residues. The

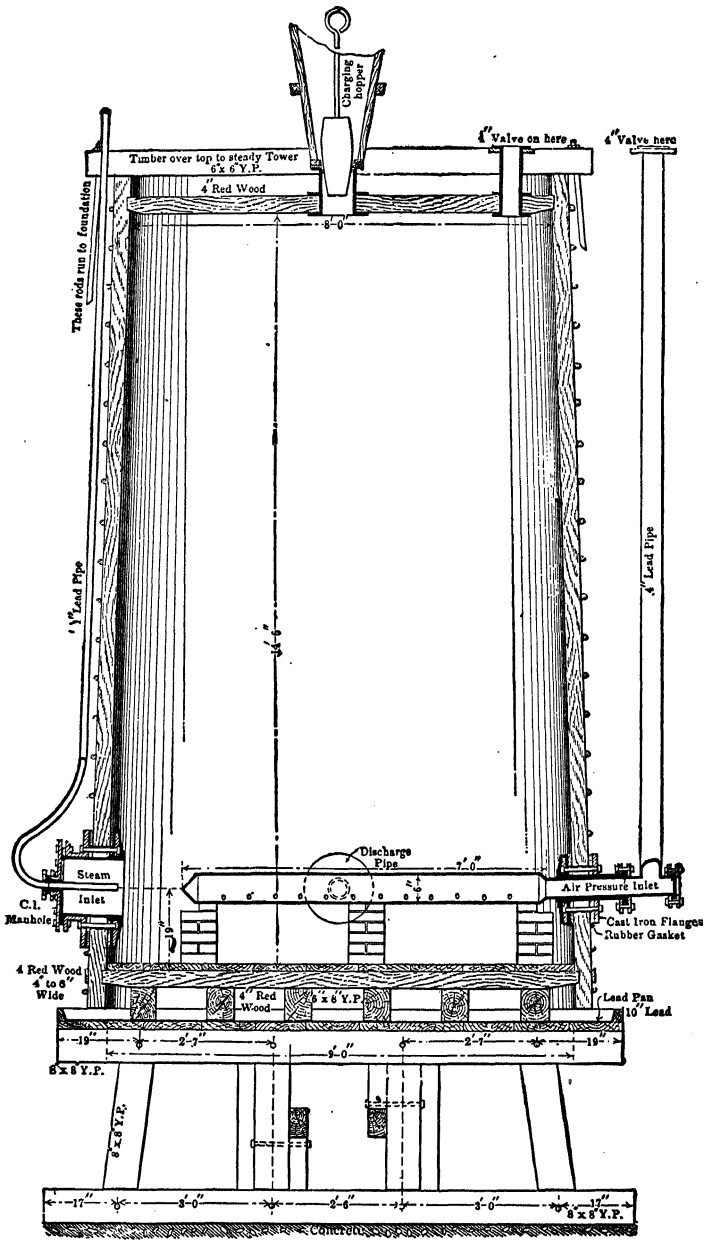


FIG. 81.—Tower for refining cupric sulphate solutions.

clarified solution flows from the press to lead lined storage tanks, from which it is elevated, by means of a pressure tank, to the purifying towers. These towers were originally made of 20-lb. sheet lead incased in a cast-iron framework, which, however, were replaced by larger ones made of 4-in. California redwood. Fig. 81 represents a vertical section of such a tower. They are made of staves 16 ft. long, 9 ft. in diameter, and are well hooped with round iron. The top and bottom are flat. The towers are firmly fastened to a strong wooden trestle, which in turn is anchored to a concrete foundation. This construction is called for to guard against the oscillating movement of the tank from the action of the contained solution, which is set in violent motion by the ascending air. Inside the tower, about 19 in. above the bottom, the 4-in. lead air pipe enters, and is connected with a perforated 6-in. lead pipe, which extends diametrically to the opposite side and is closed at the further end. Outside the tower the pipe extends upward to above the top of the tower, and thence downward to the discharge pipe of an air compressor or to an air receiver, connected with the compressor. This arrangement is necessary to prevent the solution from flowing to the air pumps if the latter be not in operation. At the same level with the air inlet, the 4-in. discharge pipe enters, which is provided with a hard-lead valve placed close to the outside of the tower. At about the same level enters a 1-in. lead steam pipe for heating the charge. The direct application of steam does not dilute the solution, because the evaporation, which is favored by the ascending air, fully equalizes the dilution by condensed steam. The top of the tower is provided with an 8-in. pipe extending through the roof for the escape of steam and air, which, however, first are made to pass through a lead-lined box provided with shelves arranged in a zigzag manner to precipitate all particles of liquor which may be carried out by the current of air. A 4-in. pipe also enters the top, which serves for filling the tower with crude copper solution. An opening in the center is connected with a small hopper which is filled with roasted matte. The upper third part of the tower is provided with glass tube gauges to control the filling. The perforations of the air pipe are only on the bottom side, to prevent the inflow of matte and precipitate. The steam pipe enters through the lid of the manhole, as the heat of the pipe affects the wood at its immediate surroundings.

The tower is filled with crude solution, leaving, however, sufficient room for the increase in volume of the solution, which immediately takes place as soon as the compressed air is supplied. A tower can be charged with about 5000 gallons of solution, and as three such charges can be refined in 24 hours the working capacity of one tower is 15,000 gallons per day. At Argentine eight such towers are in use. When the tower is filled, steam is allowed to enter, and also some air, to produce a more uniform heating of the solution. The air causes the precipitation of

some basic iron salts, but never more than half of the iron contained in the solution was precipitated, although the treatment, at times, was extended many hours. When the solution is hot (75 to 80° C.) more air is admitted, and some roasted matte from the hopper is made to drop into the tower. The violent boiling motion of the solution keeps the matte in suspension; and after 3 to 4 hours the solution will be entirely free from iron, arsenic, antimony, etc. To observe and to regulate the progress of the operation the solution is tested from time to time for iron by taking samples through a small cock inserted in the side of the tower. If between two tests the content of iron is not diminished some more matte is added. It is not necessary to test for other impurities, because the iron predominates, and by the time all of it has been precipitated, no trace of any other impurities will be found.

The cupric oxide in presence of air combines with the sulphuric acid of the ferrous sulphate, forming cupric sulphate, while the iron is precipitated as oxide, a decided advantage, as the precipitant is converted into cupric sulphate, and thus enriches the solution in copper.

The refined solution leaving the tower should not be stronger than 24 to 26° B. when hot, as otherwise it will cause trouble in the filter press, for reasons above explained. Should a concentration have taken place in the tower beyond this, the solution should be diluted. The tower is discharged into a special stir tank and from there, by means of a pressure tank, forced into a filter press. The clear and purified liquor is conveyed to the evaporating department, while the residues are subjected to an additional treatment. These tower residues are of grayish-yellow color and consist principally of precipitated iron, arsenic, antimony and some undecomposed matte, with also some basic copper sulphate. To remove the last named substance the residues are treated in a stir tank with 2.5 to 3 per cent. cold acid solution, which dissolves the basic copper salt, leaving the impurities unaffected, with the exception of iron, which is acted on very slightly.

The refined solution does not contain even a trace of silver. Whatever silver is converted into the sulphate during the roasting is precipitated in the stir tanks by the ferrous sulphate present in the solution. The residues are washed well in the filter press to remove all copper solution. The wash water is collected separately, and used instead of fresh water for the preparation of a new charge in the stir tanks. The residues contain all the silver, gold and lead of the roasted matte; they are of a dark-red color and consist mostly of iron oxide. They are sent to the lead smelting department for the extraction of the precious metals and the lead. On account of the large precentage of iron oxide and lead the residues are an excellent material for lead smelting. A large portion of the lead of the matte is converted into sulphate by the roasting, and therefore does not act much as a consumer of acid. As the roasted

matte contains 20 to 25 per cent. of its copper as sulphate, the total consumption of acid is much less than the equivalent amount contained in the blue vitriol produced.

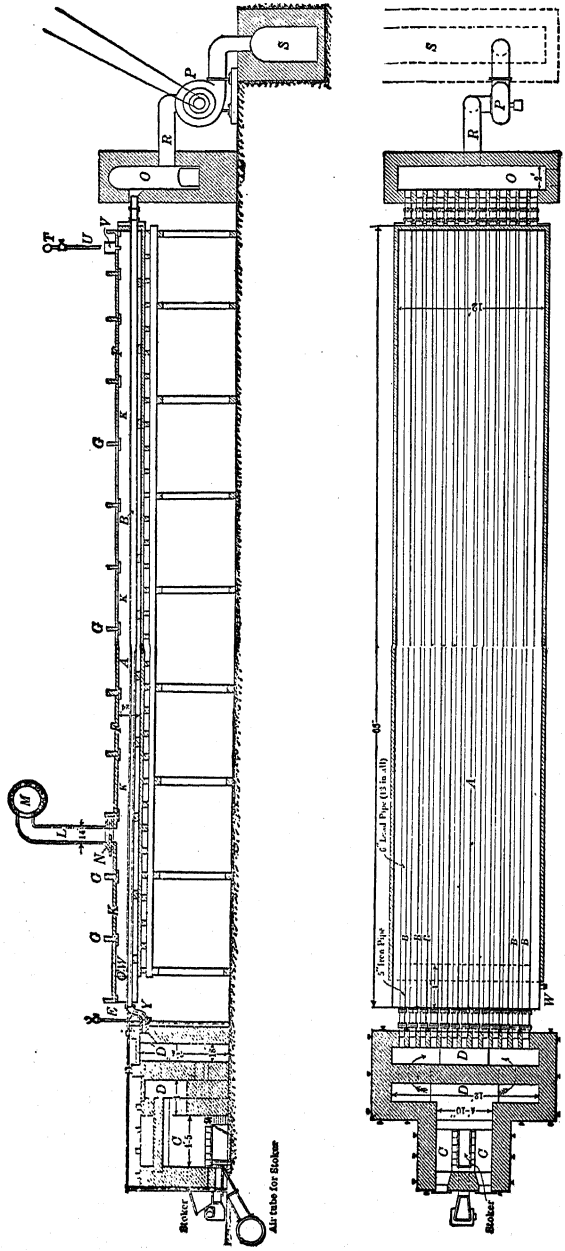
The evaporation department furnishes 90,000 gallons of concentrated solution daily. To supply this amount an improvement over the old pan evaporator with under-fire or steam coil was requisite, and as the vacuum evaporators could not be adopted an economical and effective evaporator was introduced by Hofmann, illustrated in Figs. 82 and 83. The principle observed in the construction of this evaporator is the application of the hot furnace gases in a manner by which almost a complete utilization of the heat contained in them takes place. The apparatus consists of a flat tank, wooden with the exception of a 2-ft. space at the front end, which is made of steel, so that the wood will not be in too close proximity to the furnace. The tank is 65 ft. long, 12 ft. wide and 2 ft. deep, and is lead lined, the two ends having much heavier lead lining than the sides and bottom. It is traversed longitudinally by thirteen 6-in. heavy lead pipes. These pipes rest on bricks which are properly placed on the bottom of the tank. The tank rests on wooden trestle work of a proper height to correspond with the height of the furnace. At the furnace end in each lead pipe is inserted a 5-in. pipe 4 ft. long, provided at the outer end with a flange. The iron pipe serves to protect the lead pipe from immediate contact with the red-hot gases from the furnace. They also make the connections between the lead pipes of the tank and the iron pipes of the furnace.

The furnace is comprised of the fireplace *C*, the dust chamber *D* and the distributing chamber *D'*. At a proper height in the wall of the distributing chamber nearest the tank are 13 openings, in each of which is inserted a short cast-iron pipe, 5 in. in diameter, with a flange at the outer end. Each pipe is connected with its corresponding piece of iron pipe inserted in the lead pipe of the tank by a cast-iron S-shaped elbow, *Y*, which allows the introduction of the compressed air pipe *E* for removing any accumulation of ashes in the lead pipes of the tank.

An American underfed stoker is used for the slack coal fuel and affords practically perfect combustion, which is of great importance, as otherwise the lead pipes would soon become coated with soot and lose much of their efficiency to transmit the heat to the solution.

The opposite ends of the lead pipes in the tank are connected with the brick suction chamber *O*, which in turn is connected by a galvanized iron pipe, *R*, with a suction fan, *P*, the gases being discharged into an underground flue, 8. This flue serves in common to collect the waste gases from 11 evaporators, and terminates outside the building in a brick chimney 40 ft. in height.

The top pan is closed with a wooden cover, and wooden joists, *G*, are placed across the pan about 5 ft. apart, having cleats fastened to the



FIGS. 82 and 83.—Pan evaporator, longitudinal section and plan.

lower side, as shown in Fig. 82. The spaces between the joists are covered with boards resting on the cleats and pushed together closely, but not nailed, so that the whole or part of the cover can be easily removed. About 14 ft. from the front end of the tank is a 14-in. suction pipe; connected with the main suction pipe, *M*, which crosses all of the evaporators to remove the water vapors. The main suction pipe, *M*, as well as the branch pipes, *L*, are made of wooden staves kept tight by hoops. *M* is connected with a large suction fan having the housing and wings of sheet copper and the shaft and arms of brass. This fan rapidly removes the vapor from each evaporating tank, and by its use the building, even in cold winter weather, and notwithstanding that 11 such evaporators are in operation, is entirely free from steam. A wooden stack outside the building serves for the dicharge of the fan, and the exhaust at each individual evaporator is regulated by a wooden slide, *N*, inserted below the suction pipe *L*.

Figure 82 gives the construction of the first or experimental evaporator. During the experiments it was found that the 6-in. lead pipes passing through both ends of the tank, and being burned with lead tight to both ends, did not keep their straight position, but on account of the expansion became wavy. Profiting by this experience the back ends of the other evaporators were made sloping, and the pipes, instead of passing through, passed over the edge of the back end. This allowed the pipes to expand freely, and they retained their straight position.

Close to the end of the evaporating tank and resting on the cover is the lead-lined feed box, *V*, from the bottom of which is a short pipe or nipple extending into the tank. The solution supply pipe, *T*, which crosses all 11 evaporators, is connected with the large supply tanks, and serves to convey the solution to each evaporator by down-takes, *U*. The outlet of the evaporating tank is in the side near the furnace end, about 4 in. above the hot-air pipes, *B*.

The operation is conducted as follows: The pan is first filled to the level of the outlet with the copper sulphate solution to be concentrated, the fire is then started and the stoker and suction fans set in motion. The big copper fan is not started until the solution becomes hot enough to generate steam. Some solution is added through *V* to keep the surface of the solution at the same level. When it is found that the solution near the outlet has attained the desired concentration, a continuous stream of refined solution is allowed to flow into the tank from the feed box, which starts a continuous flow of concentrated solution through the outlet. The amount of influx is regulated by frequent hydrometer tests of the solution at the outlet. The supply of fuel by the automatic stoker being regular, the heat of the evaporator is very uniform, and once having adjusted the proper influx of the weak solution the outflowing stream will be found of quite constant concentration.

The glowing hot gases entering the tubes give off the main part of their heat to the solution within a comparatively short distance from the point of entrance, and cause this portion of the solution to boil. In the passage of the gases through the tubes they gradually come into cooler regions, and are offered an excellent opportunity to give off more of their heat to the surrounding solution, so that, when they finally leave the tubes, their temperature is much below the boiling point of the solution; in fact, so low that the pipes at that end can be comfortably touched with the hand. In a tank 100 ft. or 125 ft. long the gases would leave at a temperature about that of the surrounding air, thus completely utilizing the heat of the gases.

The greater economy and efficiency of this type of evaporator, as compared with one having a steam coil or bottom fire, is apparent. The production of steam involves a considerable waste of heat, and in using it to evaporate liquids, its circulation through coils produces a large amount of condensed water at a temperature very nearly 100° C. the heat of which is generally lost. To evaporate by direct fire under the bottom of a pan is very inefficient and wasteful; and in the present case, in which no other metal but lead can be used for the pan, it requires great care and watchfulness to avoid melting the metal.

For concentrating chemical solutions which do not affect iron the evaporator described can be constructed entirely of iron and steel, and at much less cost. The pan itself, however, should always be placed in a wooden tank to prevent loss of heat by radiation.

Very fine particles of ashes settle in the longitudinal tubes, but these ashes are very light, and by turning the valve of the compressed air pipe *E*, one of which is attached to each tube, they are easily removed and blown into the chamber *O*.

The continually outflowing concentrated solution passes into a lead pipe common to all the 11 evaporators and is conveyed into a collecting tank, from which the liquor is elevated by means of a horizontal pressure tank into a system of troughs which pass over all the crystallizing tanks, of which there are 112, each of 720 cu. ft. capacity. The troughs are covered and so arranged that any individual tank can be filled. Wooden tanks, lead lined, of the same size, did not answer. By the frequent changes of temperature to which they are exposed, the lead lining continued to expand without contracting again, which caused in course of time so many leakages that it became intolerable. The present tanks are made of 20-in. thick concrete walls, which, however, do not come up to the expectation either, though they are far superior to the wooden lead lined tanks. By the sudden change in the temperature when the tank is filled with such a large volume of hot liquor, fine cracks in the walls are caused, through which, if not attended to, leakage will take place, but leakage can be prevented by plastering a little cement on the outside

of the tank. An experimental tank built of bricks, however, answered the requirements of such large crystallizing tanks. The brick walls have in the center a 2- in. space filled with a mixture of asphaltum and sand, which combines with the bottom layer of the tank, thus practically forming a tank by itself, embedded in the brickwork. When heated by the sudden filling of the tank with hot solution, the asphaltum softens, and when gradually cooled contracts without cracking.

On top of each tank are movable wooden frames supporting numerous strips of lead 5 ft. long, on which the crystals form, as well as on the sides and bottom. The solution remains 7 days in the tank. In discharging, the mother liquor is drawn off through a brass tube near the bottom, then the frames with the strips are lifted up with block and tackle attached to an overhead crawl. The crystals are knocked off from the strips with a wooden paddle and fall into the tank. The frames are then moved to one side by means of the crawl. The crystals from the sides are broken down also. The tanks are arranged in long rows intersected by several cross passages. Between each two rows is a track for transporting the blue vitriol crystals, on either side of which is a cement channel to receive and to convey the mother liquor to pressure tanks for further handling. Rails are laid in recesses near the rim of the tanks, so that the rails of the two opposite rows of tanks form a track for a hopper mounted on wheels. The crystals are shoveled with copper shovels into this hopper, which fills the push car underneath through a spout with slides in the center. As the tanks are 6 ft. deep the crystals have to be thrown at least 7 ft., and in doing so some of the crystals unavoidably fall back into the tank, frequently striking the shoveler. It was found that this was very injurious to the men, especially in summer. Their bodies became covered with deep sores, which, while not dangerous, were very painful.

To protect the men, Hofmann constructed and set in operation the device illustrated in Fig. 84. On top of the movable hopper is mounted the frame K, K, with a turntable and circular track underneath, which rests on a number of stationary wheels and is kept in place by the pin P. The object of this turntable is to make the apparatus available for the opposite row of tanks by rotating through 180 degrees. The frame K is provided with a belt elevator E, with copper cups. On the shaft F are the pulleys L and M, which drive the elevator pulley N. The elevator can be brought to a horizontal position by means of the shaft F. The lower end of the elevator is provided with the boot B, which can be brought down to within a short distance from the bottom of the tank and into which the crystals are shoveled. The power is imparted by an electric motor on the platform of the frame, which receives the electric current by an overhead wire and trolley. From the time this device came into operation

the men were protected, as they had to shovel the crystals only a short distance above the floor.

The crystals are washed in a stream of mother liquor in a trough, and conveyed by this stream into a hexagonal revolving screen, having shaft and arms of brass. The screen itself is of maple wood, perforated. There are two such screens, to make two sizes of crystals. The mother liquor with the smallest crystals, dirt and sediment, after leaving the second screen, is conveyed to an agitating tank and heated by a steam jet to dissolve the very fine crystals. The resultant solution is sent through a filter-press, the clean liquor flowing to the storage tanks. The crystals are dried in 10 brass centrifugal machines. The yearly production is about 18,000 tons of blue vitriol.

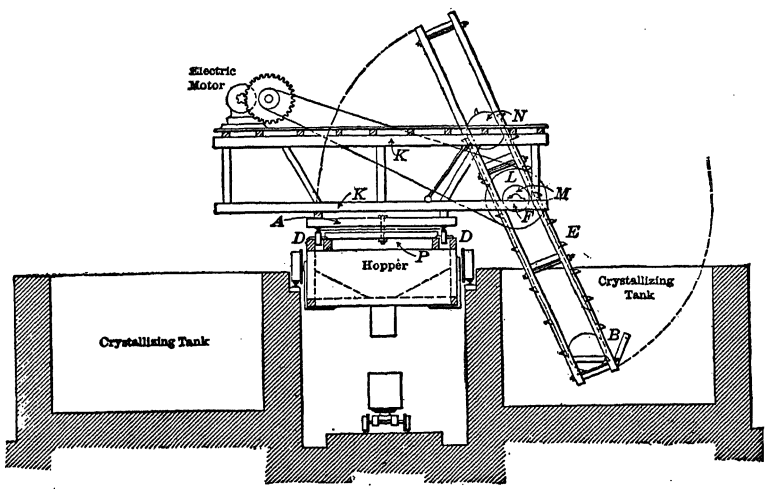


FIG. 84.—Device for descharging blue vitriol.

The crystals having been obtained from such a pure neutral solution are of a very deep blue permanent color, which is not affected by light, except in the direct rays of the sun. They do not change into a bluish-white powder, which is the case with crystals made from an acid solution.

The trade in blue vitriol demands large crystals. In crystallizing a salt solution in large tanks it will be found that, while on the strips and sides large crystals are formed, the bottom will contain mostly small crystals. As this necessitates the dissolving and recrystallization of a large portion of the bottom crystals, and consequently of quite a percentage of the total production, this peculiarity was rather annoying, and, searching for the cause, it was observed that on the surface of the cooling liquor numerous very small crystals were formed. They do not remain on the surface, but sink as soon as formed. These crystals are so small

that they cannot be seen as such, but if a good light strikes the surface, the liquor right under the surface sparkles from light reflected on these minute crystals. It can easily be observed that they sink and that new ones are continually formed, thus producing a very shower of fine crystals from the surface to the bottom. This phenomena is caused by the evaporation of the water on the very surface where the liquor is in contact with the air. By losing part of its water a very thin sheet of the solution on the very surface will become so concentrated that it has to form and drop these very fine crystals, aided by the cooling effect of evaporation and contact with the air. Following up these observations Hofmann caused a stream of water to enter the tank under light pressure and level with the surface through a flat nozzle, so that the water did not mix with the solution, but covered as such the whole surface about an inch thick. This stopped the sparkling of these minute crystals entirely, and when crystallization was finished it was found that the bottom crystals were just as good as the crystals on the sides, so that they could be mixed and treated together with the other crystals, and the tedious and expensive operation of dissolving and recrystallizing of an already finished product was entirely avoided. After this successful trial the whole crystallizing plant was equipped with a proper arrangement for this purpose, so that the operator had only to fill each tank to the given mark and then to turn on the water for a short time. The mother liquor is somewhat diluted by this method, but the advantage gained greatly outweighs the disadvantage.

CHAPTER XIX

APPARATUS AND APPLIANCES

Copper solutions are among the most corrosive substances known, and the selection of materials to be used in handling and containing the solutions is something of a problem. Of the commercial metals, iron is of course unsuitable. Copper is available in the form of sheets and pipes, but the copper itself is more or less readily dissolved, and the consequent expense of replacements and repairs would be prohibitive. Lead may be used for sulphate solutions but is quite impracticable when working on a chloride basis, for, while lead is quite indifferent to solutions of copper sulphate it is quite rapidly attacked by solutions of copper and other chorides.

Tanks.—Wood is fairly permanent, but the iron hoops have to be carefully protected, and a wooden tank, of any considerable size, which will hold either cold or hot copper solutions without leakage, is the exception and not the rule. Reinforced concrete tanks do very well if erected on ample foundations, but the concrete is attacked by the acid solutions, and hence some provision must be made for the protection of the cement. This is readily accomplished by asphalting the bottom, but the sides are not as readily taken care of. A heavy coating of hard tar for the side will answer very well for short intervals.

The usual method of constructing a rectangular wooden tank for copper solutions, is to have the sides made double, with a space of 2 or 3 in. between to be filled with tar and sand, as shown in Fig. 50, page 264. The bottom is also covered with a layer of tar and sand, on top of which is laid a course of acid proof brick as the working floor.

At Helsingborg, Sweden, the leaching vats are made of resinous pine, elliptical in shape, with the long and short diameters 10 and 6 ft. respectively, and with an inside depth of 4 ft. Both the bottom and staves are made of 5-in. wood and the whole is held together by three iron bands, 2 in. by 3 1/4 in., kept at short distances from the sides of the tank by pieces of wood so that the leaking copper solution will not disintegrate the iron.

Probably the best way of constructing the tanks and leaching vats is shown in Fig. 85 in which the body of the tank is built of re-inforced concrete, with a brick lining inside, and the space of 2 or 3 in. between the brick and the concrete, filled with asphalt. The bottom is also asphalted, so that the entire asphalting is continuous. Acid proof brick is laid on top of the asphalted bottom, which serves as the working floor.

Lead-lined tanks, which are quite largely used with sulphate solutions, should be built on solid independent foundations. Vibrations are injurious. Constructionally, lead-lined round wooden tanks are better than square tanks, but owing to the large amount of waste space in a building containing round tanks, square tanks are usually preferred.

If square, the bottoms and sides of the tanks should be built of heavy supporting timbers. The bottom timbers should be strong enough to prevent even the slightest sagging. The sides should be made of 8-in. by 10-in. or 6-in by 12-in. timbers, mortised into the bottom timbers, securely braced, and close enough together to prevent bending or bulging. This frame should be lined with 2 1/2-in. planks, which should be bolted

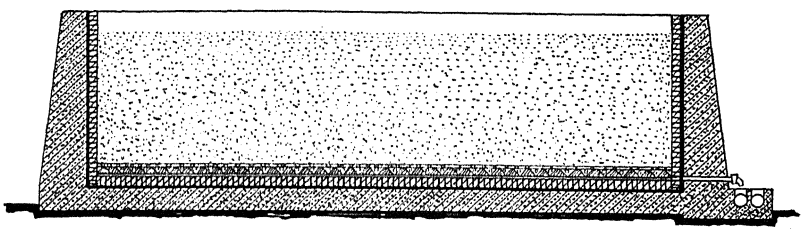


FIG. 85.—Reinforced concrete tank.

to the frame with countersunk bolts. Nails should not be used; but if used, cut nails are preferable to wire nails. After the planking is secured, it is lined with lead weighing 6 or 8 lb. per square foot. Or 8-lb. lead may be used for the bottom and about 1 ft. up the sides; above this, 6-lb. lead may be used.

The weakest part of the lead lining is always at the joint or just above it, and if the framework is not substantial enough to prevent movement, the breaks in the lead lining become serious and are a source of continual annoyance and expense. Round wooden tanks as a background for the lead lining, are better than square tanks for the reason that they are more rigid and there is no tendency toward even the slightest movement as the tanks are filled and emptied.

The sides of the lead lining of square tanks should be bolted at intervals to the timber work. This is usually done by bolting the lead to the woodwork in the usual way with ordinary iron bolts having fairly large washers, and then burning lead caps over the head and washer of the bolt, as shown as Fig. 86; or an iron bolt having the head encased in cast lead, may be used, as shown in Fig. 87. The edges of the cast lead head should then be burned to the lead lining of the tank. The bolting of the lead lining to the wooden frame prevents undue movement, to which most of the breaks and leaks in lead-lined tanks may be attributed.

The tanks should not be too deep; from 5 to 7 ft. in the clear is a good

height. Fewer larger tanks are better than more smaller ones of the same capacity. It is best to make the tanks shallow and large in area,

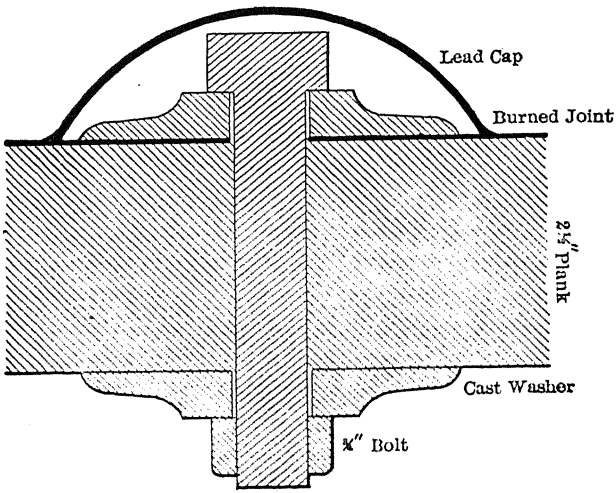


FIG. 86.—Detail of lead lined tank construction showing method of bolting lead lining to wood frame.

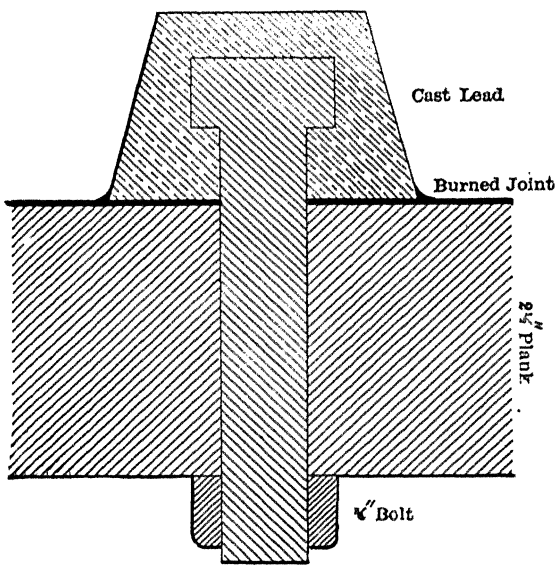


FIG. 87.—Detail of lead lined tank construction showing method of bolting lead lining to wood frame with iron bolts protected with lead.

rather than deep and of smaller area. The settling or leaching in large shallow tanks is much more readily accomplished and the repairs are less.

Settling tanks usually have two openings in the bottom; one of these openings is surrounded by a collar 4 to 6 in. in diameter and 6 to 8 in. high, through the top of which the clear settled solution is drawn, leaving the slimes in the bottom of the tank. The other hole is flush with the bottom, so that when the tank requires cleaning the accumulated slimes are swept through the hole. The entire tank should drain slightly toward this hole to facilitate cleaning.

Both holes are provided with a collar on the outside to which is clamped a short piece of rubber hose, so that the flow of solution may be regulated or shut off by a pinch clamp working on the hose. This arrangement is preferred to rod and rubber stopper working from above.

The side corners of rectangular tanks should be chamfered, and the lead should fit snugly against the wood.

All joints and connections should be burned; no joints or connections should be soldered.

The following table gives the thickness and corresponding weights of sheet lead, which is convenient for reference in connection with lead lining of tanks.

SHEET LEAD

Thickness,	Weight.
3/64 in.	2 1/2 lb.
1/25 in.	3 lb.
1/16 in.	4 lb.
1/14 In.	5 lb.
1/12 in.	6 lb.
1/10 in.	7 lb.
1/8 in.	8 lb.
5/32 in.	10 lb.
3/16 in.	12 lb.
1/4 in.	16 lb.
3/8 in.	24 lb.

Conducting Solutions.—For conducting solutions, wooden troughs, lead pipe, or earthenware may be used. Lead pipe is available for sulphate but not for chloride solutions. Acid proof rubber hose may be used for both sulphate and chloride solutions, but is rather expensive, and deteriorates quite rapidly. Hard rubber piping is unaffected by any copper solution, but is very expensive, breaks easily, and once broken, difficult to mend. Lead-lined iron pipes are used and give satisfactory results in handling mine water at Butte. Enameled iron piping is also made which is said to withstand the corrosive effects of either acid or alkali solutions, and may be used under pressure equal to that of ordinary iron piping.

Wooden troughs are best made as shown in Fig. 88 by bolting the sides to the bottom piece. The bolts go through auger holes in the

bottom piece, and have cast washers on both sides. The distance between the bolts should not be more than 4 to 6 in., and the cast-iron washers should be reasonably large. In fitting lengths together, the joint is made by cutting the ends off square, inserting a rubber gasket between them, and then drawing the ends together with an iron yoke fitted to the end of each section, as shown in Figs. 89, 90 and 91. The yokes are made of cast iron, and set into 1/2-in. grooves around the sides and bottom of the trough, and provided with holes to screw them to the wood. By means of bolts, from one casting to the other, the ends may be tightened as desired. Troughs are available only where the solution is not under pressure.

If lead pipe is used the lengths may be connected to one another either by burning, or by flange unions without burning. To make a

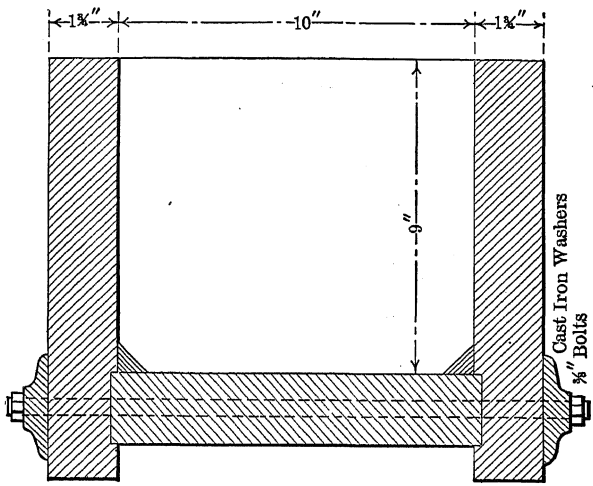


FIG. 88.—Detail of trough construction.

flange connection with lead pipe the ordinary iron flanges are made smooth and the sharp corners rounded in a lathe. The lead is then swedged so that when the pipes are brought together; the lead flanges will be securely bolted between the iron flanges, thereby protecting the iron flanges, and making the lead pipe continuous, as shown in Fig. 92. The joints can be made tight without a rubber gasket, but if a gasket is used it should be of pure rubber. Ends of the pipe may be closed in much the same way by flanging the end of the pipe, and inserting a lead disc to protect the outer iron flange, as shown in Fig. 93. Only the heavier weight lead pipes should be used. The following table gives for convenient reference, the standard sizes and corresponding weights of lead pipe.

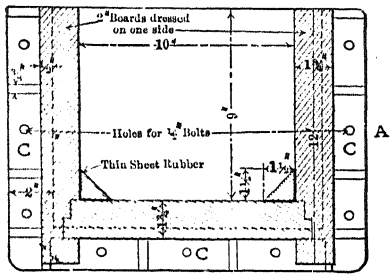


FIG. 89.

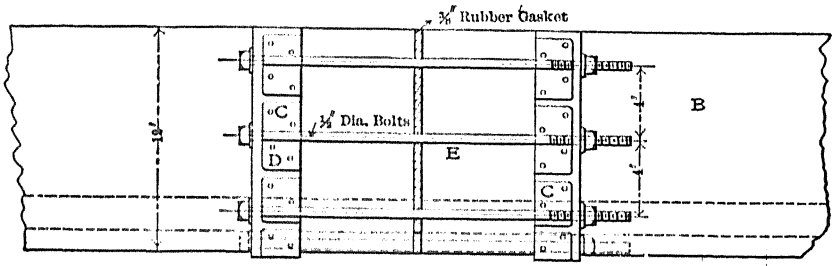


FIG. 90.

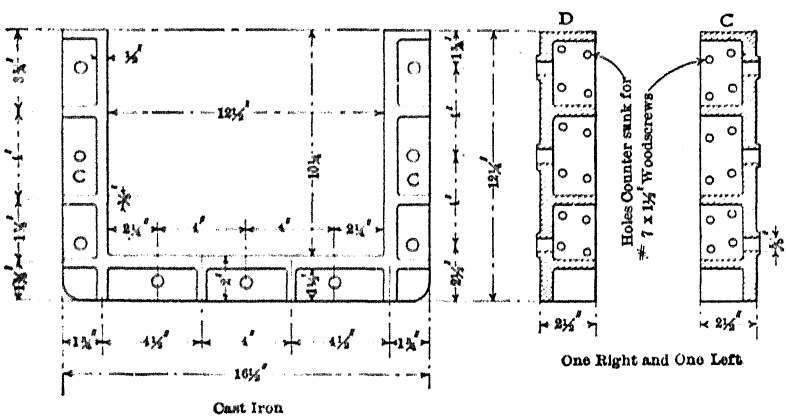


FIG. 91.

FIGS. 89, 90, 91.—Details of trough construction. Fig. 89, cross-section of trough; Fig. 90, connection of troughs; Fig. 91, trough union.

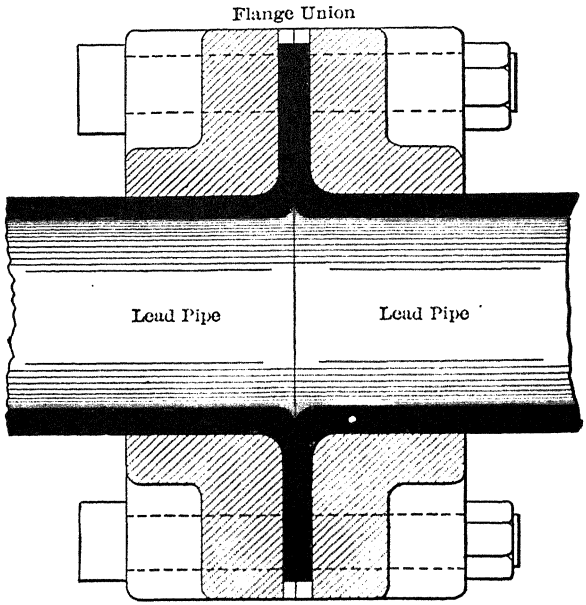
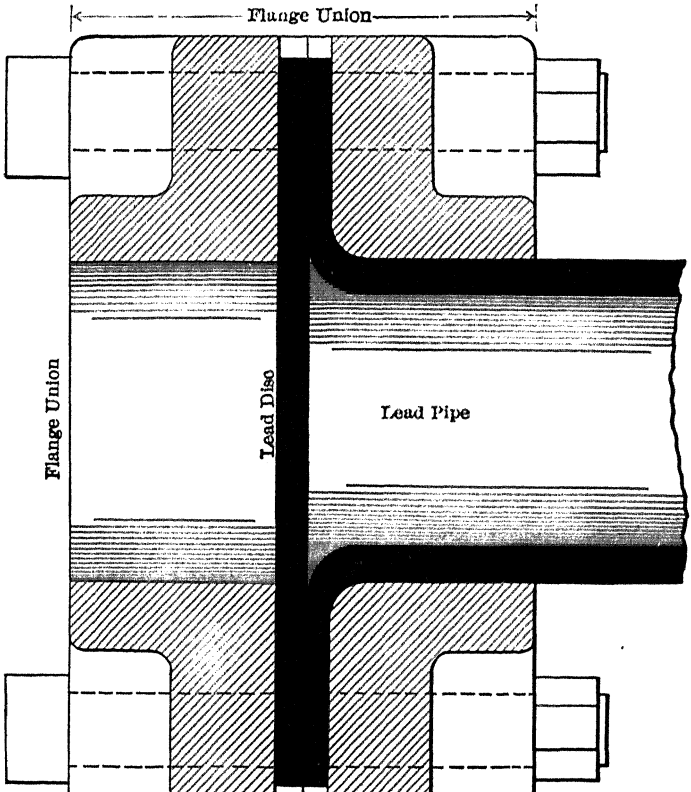


FIG. 92.—Lead pipe connection with iron flange union.



LEAD PIPE. WEIGHT PER FOOT

Size	X Light		Light		Medium		Strong		X Strong		XX Strong	
	Lb.	Oz.	Lb.	Oz.	Lb.	Oz.	Lb.	Oz.	Lb.	Oz.	Lb.	Oz.
3/8			0	12	1	0	1	8	2	0		
1/2			1	0	1	4	1	12	2	8	3	0
5/8			1	12	2	0	2	8	3	0	3	8
3/4	1	8	2	0	2	4	3	0	3	8	4	0
1	2	0	2	8	3	4	4	0	4	12	5	8
1 1/4	2	8	3	0	3	12	4	12	6	0	6	12
1 1/2	3	8	4	0	5	0	6	0	7	8	9	0
2	4	0	5	0	7	0	8	0	9	0	12	0
2 1/2			6	0	8	0	14	0	17	0	22	8
3	4	12	6	4	9	0						
4	5	0	8	0	10	0						

With lead-lined iron pipe the connections are made as shown in Fig. 94 to prevent the solution from coming in contact with the iron.

Open conduits, lined with lead, are largely used to convey solutions, but these give more or less trouble and are difficult to repair.

Ordinary stoneware pipes may be used for solutions not under pressure; modification is required to withstand either the pressure outward, or the suction inward. When stoneware pipes are required to

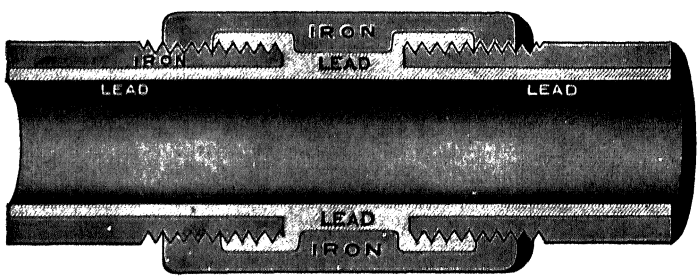


FIG. 94.—Method of making joints with lead lined iron pipe.

work under pressure, the lengths are usually flanged and the faces of the flanges ground to make a tight fit. The flanges are then bolted together with a yoke, as shown in Fig. 95 for square flanges, and Fig. 96 for conical flanges. Such piping, if properly installed, is practically indestructible. The iron should be well painted with acid-proof paint, to prevent any possible attack of the copper solution on the iron from the outside.

Regulating the Flow of Solution.—This, for lead pipe, is readily accomplished by inserting a short piece of pure rubber hose between two ends of the lead pipe line, and using a hose clamp, as shown in Fig. 97 by which the solution may be regulated as desired or shut off entirely. If stoneware pipe is used, stoneware faucets may be inserted anywhere

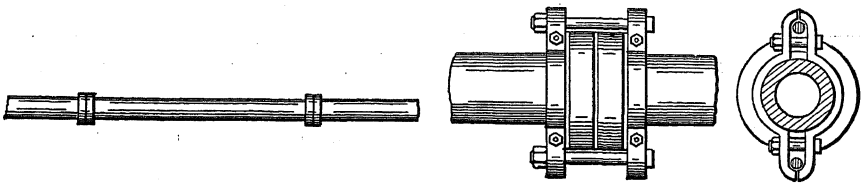


FIG. 95.—Method of joining stoneware pipe with square flanges.



FIG. 96.—Method of joining stoneware pipe with conical flange.

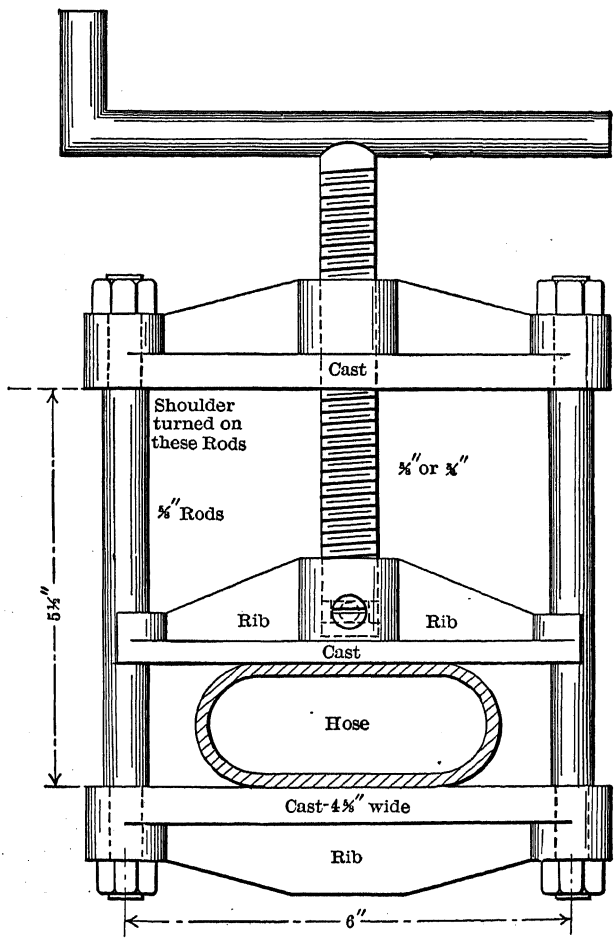


FIG. 97.—Iron clamp for regulating the flow of solution through rubber hose, for size varying from 1 1/2 to 3 inches.

in the line as desired. In such cases it is best to use the block faucets as shown in Fig. 98 and the method of connecting as shown in Fig. 99 whereby the faucet is firmly bolted between two lengths of flanged stoneware pipe. Both stoneware and vulcanized rubber faucets are regularly made for regulating the flow of corrosive solutions.

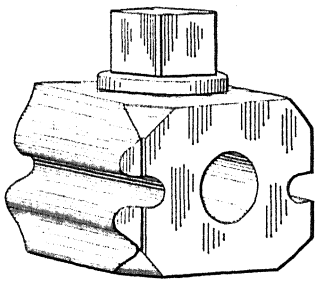


FIG. 98.—Stoneware block faucet.

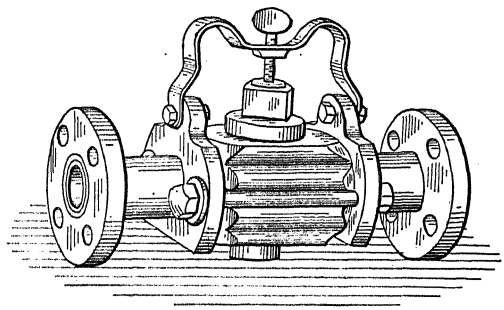


FIG. 99.—Method of connecting stoneware pipe with stoneware block faucet.

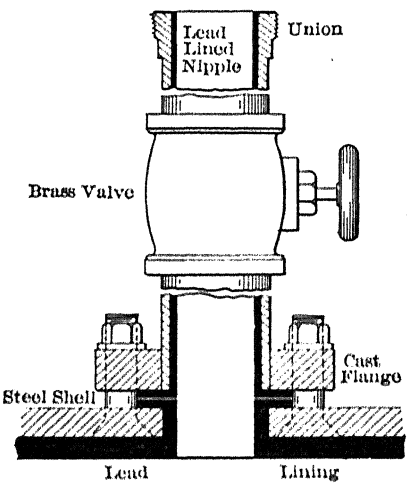


FIG. 100.

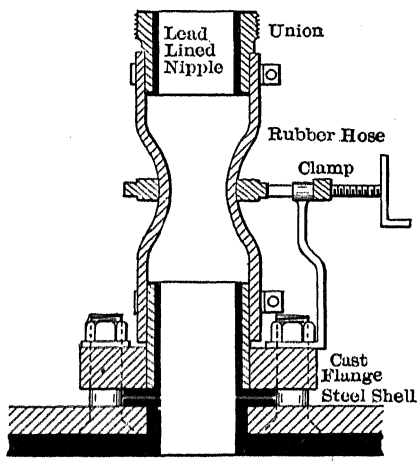


FIG. 101.

FIGS. 100 and 101.—Connections with lead lined iron tank. Fig. 100 shows connection for brass valve. Fig. 101, connection for hose clamp.

Fig. 100 shows connection with lead-lined iron tank and brass valve for regulating the flow of solution. This method is applicable to solutions not exceedingly corrosive, and the brass valves are not readily attacked. Under such circumstances it is more satisfactory to occasionally replace the valve than to use other methods of regulating the flow. Fig. 101 shows connection between lead-lined iron tank and hose and clamp for regulating the flow of solution. In both Figs. 100 and 101 the ends are

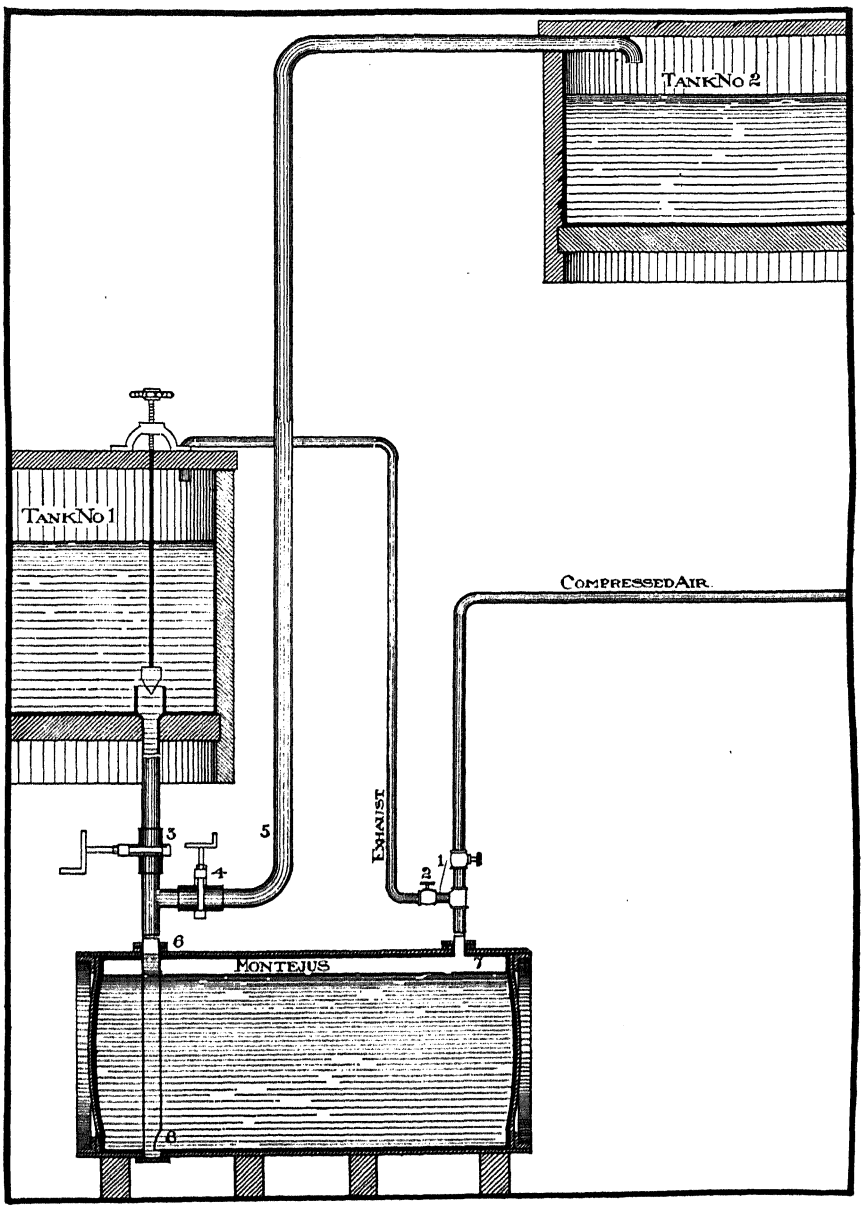


FIG. 102.—Montejus tank arrangement for elevating corrosive liquids.

arranged for hose connections, by using an ordinary malleable iron pipe coupling. This is done by lining the nipples attached to the coupling with lead, and inserting a rubber gasket between the lead ends of the two nipples, thus preventing leakage and preventing the solution from coming in contact with the iron, or threads of the coupling.

Elevating Solutions.—In elevating solutions ordinary pumps cannot be employed. Solutions may be elevated either by

1. Montejus tanks
2. Air lifts
3. Stoneware pumps
4. Rubber pumps.

Montejus Tanks.—These are usually made of thick sheet steel, lined with lead. Externally they have the general appearance of a steam boiler. Their capacity varies somewhat with the size of the plant. A Montejus holding 5 to 6 tons of solution might be considered about the average size and one which is very convenient. They should be abundantly strong to withstand the pressure necessary to elevate the solution to the height desired. Usually the sheet steel is 3/8 in. thick for the cylinder and 1/2 in. for the ends. The tank should be made with butt joints and countersunk rivets, so as to have the interior perfectly smooth for the lead lining. Both ends should be removable. Frequently they are made with one end fixed; this is a mistake, since it makes repairs and replacing of lead ends very difficult. The lead lining should not weigh less than 12 or 14 lb. per square foot, and be frequently bolted to the steel shell. Fig. 102 shows a section of the usual design of a lead-lined Montejus for elevating solutions unaffected by lead.

To elevate solutions with a Montejus, the compressed air valve 1, is supposed to be closed and the exhaust valve 2 open. Pinch clamp 4 in the lead pipe line leading to the elevated solution tank is closed if there are more than one Montejus connected with the solution line. If there is only one it may always remain open. Pinch clamp 3 in the lead pipe line leading to the supply tank is then opened and the solution flowed in until the Montejus is full. As the tank fills the air escapes through the exhaust pipe, which on account of the likelihood of solution being forced up through it, is returned to the supply tank. There is no danger of getting too much solution in the Montejus, for even if it enters the exhaust pipe or solution line, no harm will result excepting perhaps corrosion of the metal exhaust valve. When the Montejus is full, clamp 3 in the line leading to the supply tank is closed; clamp 4 is opened and the exhaust valve 2 is closed. The compressed air is then turned on slowly until equilibrium is established, when the valve may be opened wide. The pressure of the air on the surface of the liquid forces it through the end hole in the pipe in the bottom of the Montejus, into the line leading to the elevated tank to which the solution is being lifted.

When the Montejus is almost empty there is a peculiar sound of air escaping with the solution. The compressed air valve is then closed. The expansion of the air in the Montejus is sufficient to elevate the small remaining quantity of solution. The exhaust valve is then again opened, but most of the air will have escaped through the solution pipe. This operation is repeated until the desired quantity of solution is elevated.

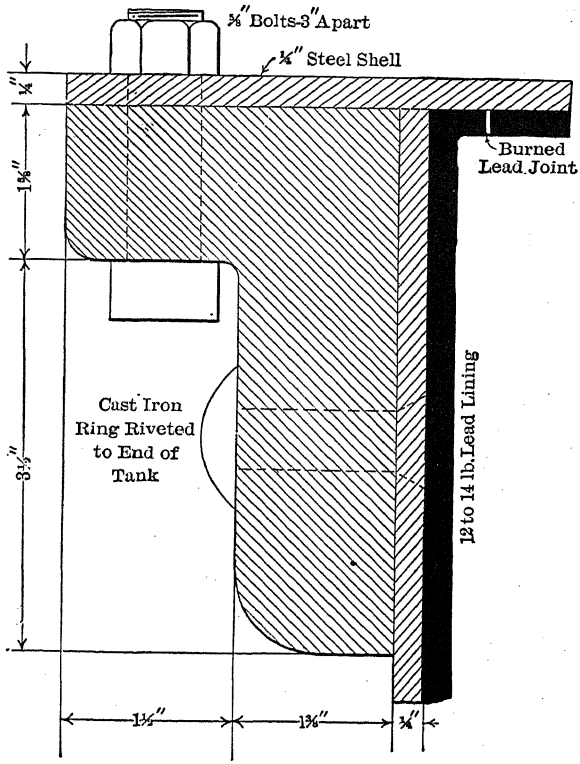


FIG. 103.—Detail, Montejus lead lined tank. End construction.

The ends of the Montejus are usually its weakest parts. If the solution is to be elevated to a considerable height, the ends are likely to develop a weakness, unless very substantially built. The best way to build them is to reinforce the ends with a heavy cast-iron ring as shown in detail section, Fig. 103. The cast-iron ring is riveted to the sheet steel end with countersunk rivets on the inside. The entire end is then bolted to the circumference of the steel shell, and is removable with but little trouble.

Fig. 104 shows a detail section of method of bolting the lead lining to the steel shell; Fig. 105 a detail section of the solution pipe connection at 6, and Fig. 106 a detail section of the pipe connections with the shell

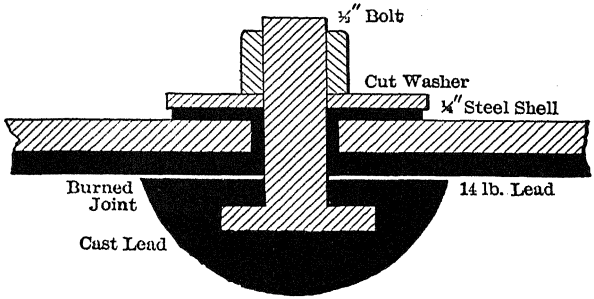


FIG. 104.—Detail of Montejus lead lined tank construction. Showing method of bolting lead lining to steel shell.

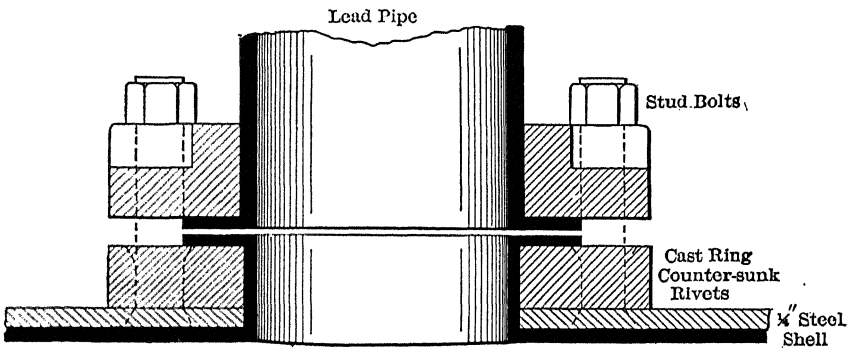


FIG. 105.—Detail of Montejus lead lined tank construction. Showing solution pipe connection at top.

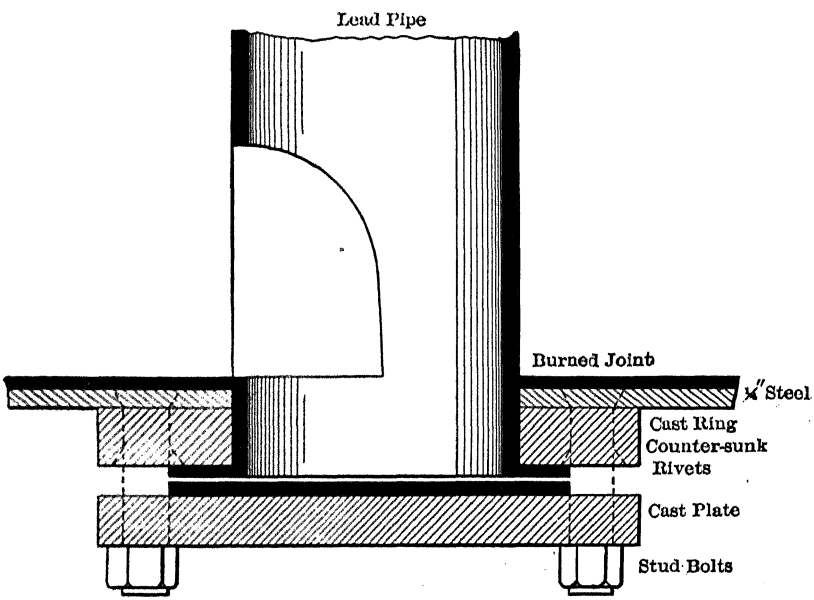


FIG. 106.—Detail of Montejus lead lined tank construction. Showing solution pipe connection at bottom.

at 8. The object of bolting the pipe to the shell at 8 is to prevent vibration of the end and thus prevent its early destruction. Sometimes the lead pipes, instead of being bolted to the shell are burned to the lead lining, but this is an inferior way of doing it.

The objection to this type of Montejus is that it is not automatic, as ordinarily built. It takes about 5 minutes to fill a Montejus of 5 or 6

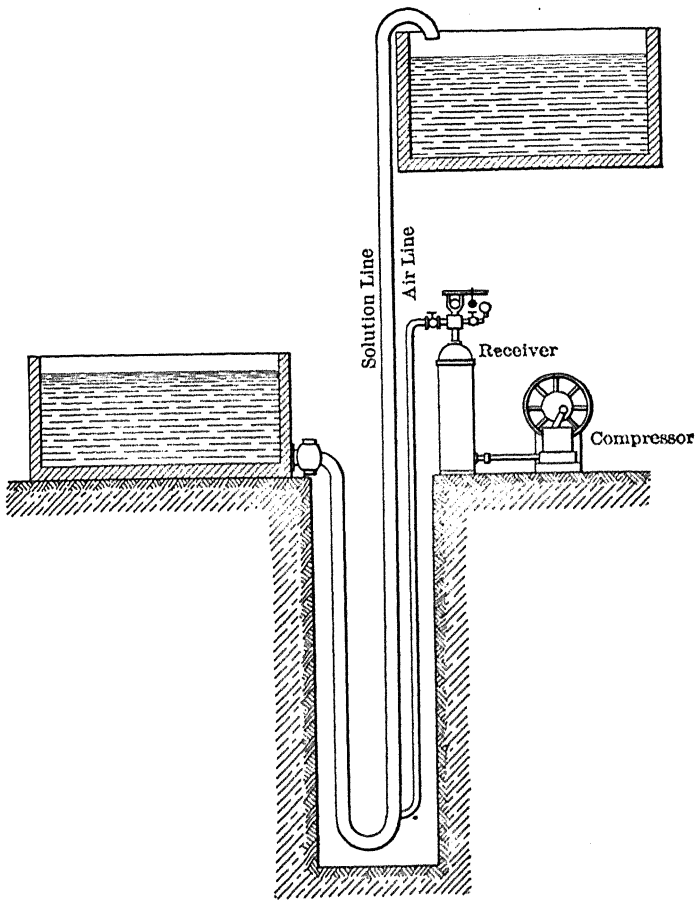


FIG. 107.—Air lift for handling corrosive solutions.

tons capacity, and about 5 minutes to empty it through a 5-in. pipe, under the average conditions. The time will of course vary with the height of solution at which it flows into the Montejus and the air pressure used in forcing it out.

Automatic Montejus apparatus is made in stoneware for lifting solutions which act on lead. These are built to withstand a pressure of from 60 to 75 lb., and have capacities ranging as high as 225 cu. ft., per hour.

Air Lifts.—One of the best ways of elevating corrosive solutions by compressed air is by the air lift system. It is especially applicable to unfiltered solutions, containing grit, that might have an injurious effect on either metal, stoneware, or rubber pumps. The apparatus is simple, cheaply installed, and entirely automatic. Fig. 107 shows the usual arrangement of the air lift for corrosive solutions. If lead is unaffected by the solution, the entire apparatus may be made of lead. If lead is unsuited, stoneware may be used.

The compressed air line, above the level of the standing solution, may be made of the ordinary iron pipe, with the ordinary brass valves to regulate the flow of air. The proper proportion of the air pipe to the solution is about 1 to 3. The following sizes of air and corresponding solution pipes will be found to give satisfactory results.

AIR LIFT

Air pipe, in.	Solution pipe, in.
1/2	1 to 1/2
3/4	2 to 2 1/2
1	3 to 3 1/2
1 1/2	4
1 3/4	5
2	6

To get the best results, the standing level of the solution in the pipe should equal the height to which it is to be lifted, from the same level. Good results have obtained in which the standing level of the solution is two-thrids that of the lift. If, for example, the solution is to be elevated 30 ft. the best results are obtained when the standing level of the liquid is 30 ft. above the air inlet, although good results may be obtained with the solution level at only 20 ft. The amount of air required to lift the liquid varies considerably with the installation. Roughly speaking, it might be said that 1 cu. ft. of air will raise 8 lb. (1 gallon) of liquid, although in well designed lifts it may elevate as much as 10 and 12 lb.

The principal on which the air lift works is that of the buoyancy of compressed air, which also forms a partial vacuum very similar to the suction in an ordinary pump. The propelling force in an air lift is due to the difference in specific gravity between the air and liquid. Taking the weight of the liquid, for example, as the same as that of water, or as 1, the specific gravity of air is 0.0012. Compressed air, on account of its elasticity, when liberated under water is very buoyant, and as it expands, forms large bubbles, which act more or less like pistons, and force the liquid upward. The bubbles as they ascend, on account of the removal of the weight of liquid above them, expand, until finally they issue at almost atmospheric pressure. It would be seen that the liquid which is removed by the air, lessens the weight in the lift pipe, which in turn

causes the solution to flow in at the bottom because of the greater weight of solution in the supply pipe.

The arrangement for introducing the air into the solution line is practically immaterial. It may enter from the side or at the center with equally good results.

In operation, air lifts are entirely automatic, and large volumes of solution may be handled cheaply for moderate heights. J.E. Rothwell gives the working of an air lift with which 90 tons of solution was raised 18 ft. in three hours, by using a 4-in. pipe with a 1.5-in. air inlet, and using the air at 15 lb. pressure.

If the location of the mill is such as to make it very expensive to get the necessary fall, the solution may be raised in two or more stages, by using the first to get the nececessary height of solution for the second. If, for example, it is desired to raise the solution 30 ft. and a drop of only 10 ft. is available, then by first raising the solution 10 ft. which with the drop gives 20 ft., which height may then be used to raise it the desired 30 ft. In such cases the cost of installation will be cheaper than when a single stage of lifting is employed, but the expense of operating will be more. In sinking a shaft in the ground for the required depth of solution, it is well to make it large enough for a man to enter, and permit of inspection at all times.

In working air lifts, storage tanks, to equalize the flow of solution, are not necessary. If the air is once properly regulated, when the solution is flowing into the lift it will be elevated; if there is none flowing, a small loss of energy, due to wasted air, is the only harmful result.

In a well-designed air lift the combined efficiency of the compressor and lift should be about 70 per cent., and in cases where a comparatively small amount of liquid is being raised continuously the efficiency of compressor and lift should be 30 to 50 per cent.

In a well-designed lift the nozzle should be connected directly to the compressor in order to use air compressed to the minimum pressure required. The lift should not be used at more than one-half of its maximum capacity. The size of the nozzel should be sufficient to keep the air entry head small.

Stoneware Pumps.—Stoneware plunger pumps may be used for elevating solutions, in which all the parts coming in contact with the corrosive solutions is made of stoneware, bolted together and strengthened with iron. The supporting frame, pulleys, and shafting, are all of iron. These pumps are either horizontal or vertical, with single or double cylinders. Fig. 108 shows a vertical double cylinder pump. These pumps are made in various sizes, to handle from 50 to 700 cu. ft. of liquid per hour.

[1] Min. Ind., Vol. IX, page 368.

Centrifugal pumps, made entirely of stoneware, are also made, and may be used for delivering large volumes of solution to moderate heights.

Rubber Pumps.—These pumps, Fig. 109, like those made of stoneware, are unaffected by copper solutions. All parts of the pumps which come in contact with the corrosive liquid, are made of hard rubber; these are held by, and mounted on, iron parts, which take all the strain other than internal pressure due to head of discharge. These pumps are made for either steam, motor, or belt drive, and in sizes of 2 1/2-in. cylinder with 4-in. stroke, up to 6 in. cylinder with 10-in. stroke.

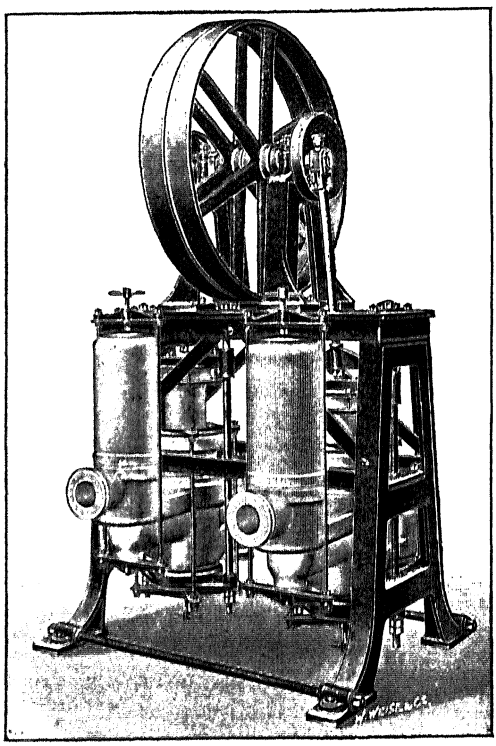


Fig. 108. Stoneware double cylinder pump.

Pressure Tanks.—These are used in connection with the settling and decanting of solutions, the slimes of which are recovered for their valuable metal content, or filtered for their soluble metal values. If copper ores contain precious metals which may be separately precipitated either with hydrogen sulphide or sodium sulphide, the precious metal values accumulate until it is desired to clean up, when the slimes are swept into the pressure tank and forced to the filter presses. If the copper solutions are settled before precipitating, the slimes may be similarly

treated and washed. These slimes may contain lead sulphate, as a valuable by-product, in the operation of the Longmaid-Henderson process.

Fig. 110 shows the usual arrangement of a pressure tank installation. The solution is flowed into the tanks where it is settled or precipitated. In either case it is not necessary to pass all the solution through the pressure tank; but the settled solution is passed through the decanting pipes directly into the decanting press, and this is continued until sufficient slime or precipitate has collected to make the clean-up desirable or necessary. If allowed to accumulate too long, some of the slimes may pass over the collar in the bottom of the tank leading to the decanting

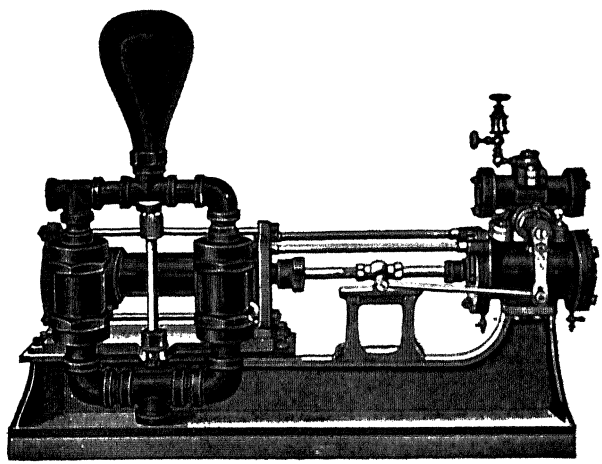


FIG. 109.—Rubber pump (steam driven).

line and thus prematurely clog the decanting press. If desired, as frequently happens, the solution may be decanted through the pressure tank. After sufficient slime or precipitate has accumulated, the outlet in the bottom of the tank is opened and the precipitate or slime is swept into the pressure tank, which at the same time is allowed to flow through the clean-up press. When the pressure tank is full and the press has become clogged or slow in filtering, the solution inlet and air exhaust pipes are closed, and the compressed air turned on. This forces the slimes into the press and filters them. Water is then introduced into the pressure tank and forced through the press until the slime has been sufficiently washed. The press is then opened and the filter cake removed.

The pressure tank is usually made of 3/8-in. steel sheet, with 1/2-in. dished head and bottom. The entire steel shell is then lined with 8-lb.

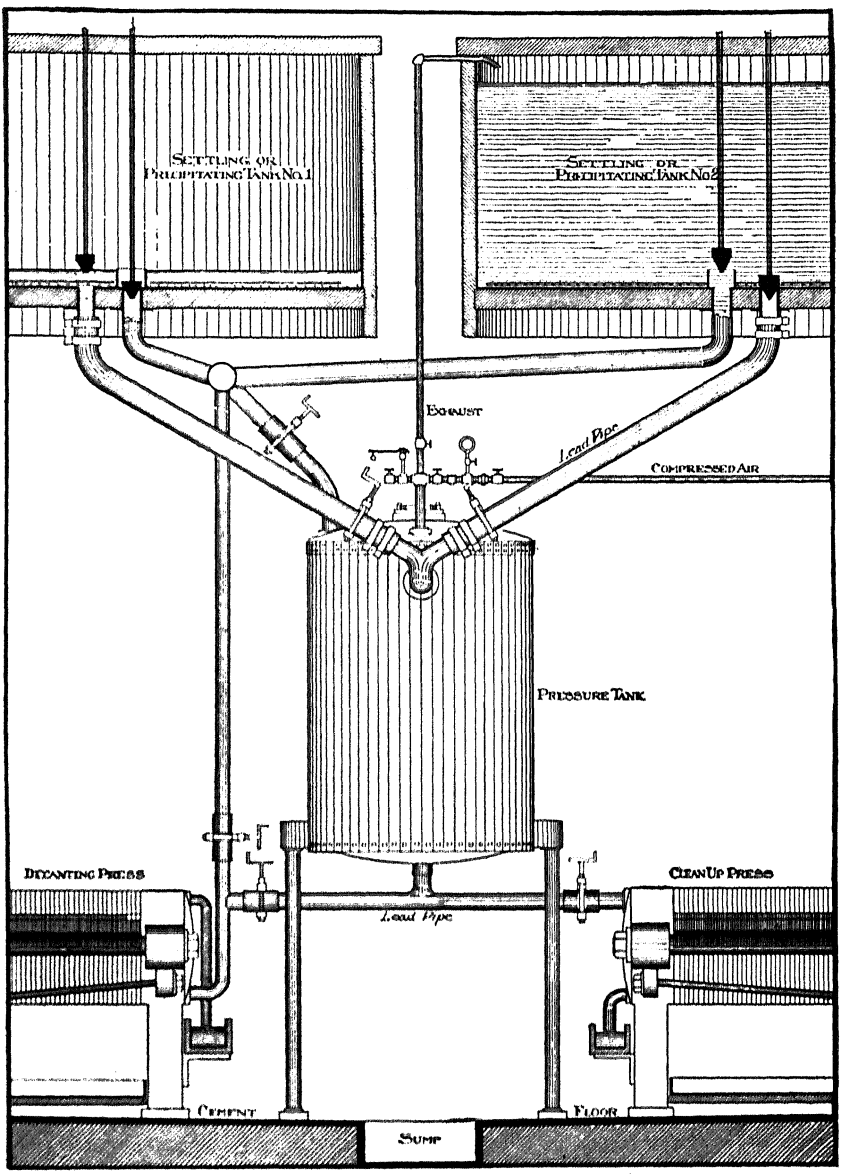


FIG. 110.—Pressure tank installation for handling corrosive solutions.

lead. All the pipes and connections are usually made of lead with all joints and connections burned.

Ore Agitation and Filtration.—It is generally conceded that during the solvent treatment of the ore, agitation gives more satisfactory results than percolation. The cost is usually greater. Some ores, like roasted pyritic cinders, or quartzite or sandstone carbonates, leach so well that it may be a question if agitation presents any advantages. Other ores cannot be conveniently percolated under any conditions, but all ores, if properly ground, can be agitated. Agitation is more expensive than percolation, and this applies with greater force to acid than to alkaline solutions, and more pertinently to copper solutions than to solvents ordinarily used in the hydrometallurgical processes for the extraction of gold and silver. The greatest difficuly in agitation, comes in subsequently clarifying the solutions preparatory to precipitation. If the ore is percolated, the solution issues from the leaching vat perfectly clear and is ready for precipitation without further clarification. Acid solutions do not filter or settle as well as alkaline solutions, and this is true no matter what the particular method of ore treatment may be, or the character of the ore.

If the ore is agitated, the greatest difficulty is encountered in filtration or decantation. In the cyanide process for the extraction of gold and silver from its ores, this problem has been successfully solved by many of the pressure or suction filters; but with acid solutions these filters would have to be radically modified to adapt them to copper processes. The problem is not an easy one, for while asbestos cloth would stand the action of copper solutions satisfactorily, the construction of the filter frames, pipes, and connections, of a material that will be strong enough and that will not be rapidly corroded, presents serious difficulties. It is certain than none of the filters at present used in the cyanide process are applicable to acid copper processes without considerable modification.

However, the problem of clarifying corrosive acid solutions is not at all insurmountable, or even serious. This is practically evidenced by the chlorination treatment of from 800 to 1000 tons of Cripple Creek ore daily, in which all the solutions are clarified by settling and decantation, so that the impurities are not enough to prevent the convenient melting down of the gold precipitate in graphite pots. For the present, at least, the most feasible method of clarifying solutions resulting from the treatment of copper ore by agitation, is by settling and decantation. This may be done either in the agitation apparatus or in special settling tanks; the best scheme would probably be a combination of the two, in which the solution is partially settled in the agitator, to make washing more effective, and then settling the solution in large tanks where it will have ample time for thorough clarification. The clear solution may

then be decanted, and the slimes allowed to accumulate until it is desired to clean the settling tank.

The wash waters, in any case, will not be as difficult to filter as the concentrated copper solution, so that filtration of the wash waters may take place quite readily through sand filters, or in some form of pressure or suction filter.

If the ore is treated by agitation, stir tanks may be conveniently used, as for example, those used by Ottokar Hofmann, in the treatment of copper-lead matte, shown in Fig. 77, page 437. Air agitators, somewhat similar to Pachuca tanks may also be conveniently used, but with modifications to adapt them to the treatment of corrosive solutions.

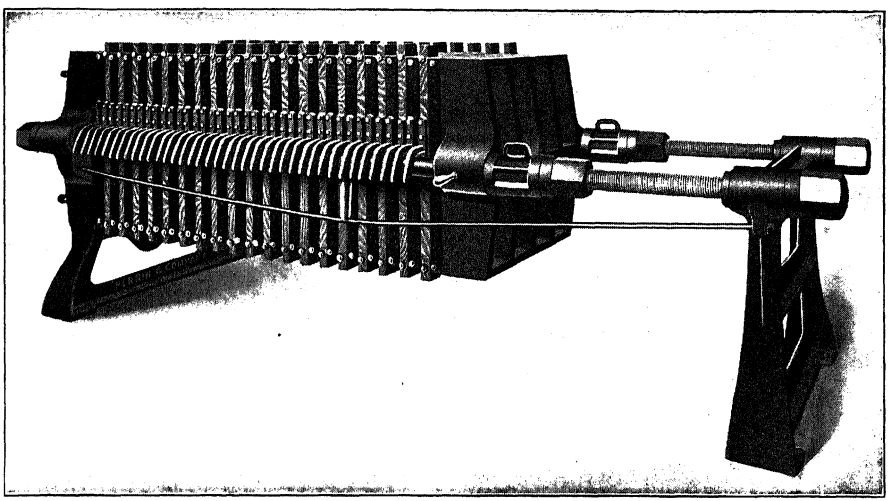


FIG. 111.—Filter press with wood plates and frames.

Filter Presses for Filtering Acid Copper Solutions.—In filtering acid copper solutions, wooden plates and frames are used instead of iron; otherwise the presses are essentially the same as any other press using iron plates and frames. The working admissible pressure, however, is considerably less, varying from 20 lb. per square inch for 18-in. plates to 5 lb. per square inch for 36-in. plates. The thickness of the cake will vary from 1 in. in the smaller sizes to 1 1/2 in. in the larger sizes. In the smaller presses there are usually 25 plates and 26 frames, while in the larger presses there are usually 40 plates and 41 frames. The filtering area will vary from 40 sq. ft. in the smaller sizes to 450 sq. ft. in the larger sizes. Fig. 111 shows a filter press with wooden plates and frames. Fig. 112 shows in detail a square wood plate and a square wood frame. For sulphate solutions lead plates and frames may be used, and the presses may be lead lined.

Construction of Floors.—The entire leaching and precipitating plant of a wet copper installation should be well cemented and covered with a substantial layer of asphalt. Copper solutions are more difficult to contain than water or cyanide solutions, and it is better to make provision to catch all possible leakage than to depend on not having any. Both the leaching and precipitating rooms should drain to a sump from which the solution can readily be pumped into the circuit. Copper solutions rarely freeze, so that there is not the same trouble with leakage on that account, as with other solvents.

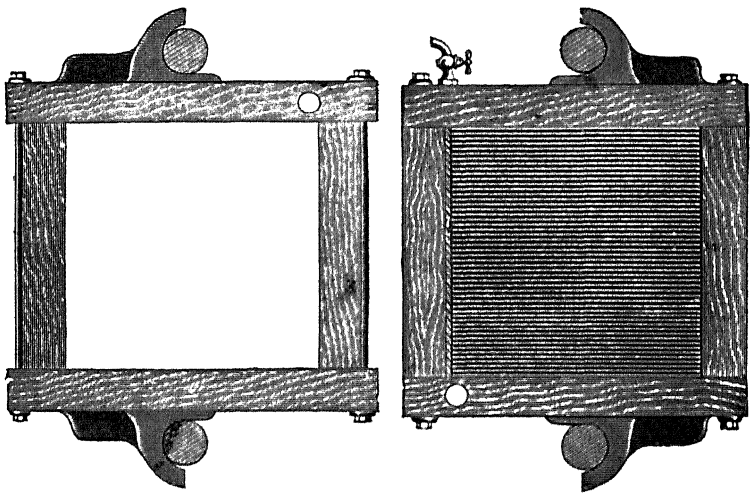


FIG. 112.—Details of wood filter plates and frames.

CHAPTER XX

POWER DATA

The cost of power, especially for electrolytic processes, is a fundamental factor in determining the cost of the copper extracted. The amount of copper deposited electrolytically, is more or less proportional to the power consumed, and hence, the cost of power not only determines largely the cost of the copper, but also to a very large extent the most economical current density to be employed.

There will usually be three methods available for generating power:

1. Steam,
2. Producer gas,
3. Water power, accompanied, usually, by electrical transmission.

Electrolytic precipitation offers ideal power conditions because the power consumed is uniform and in constant use for 24 hours in the day. With careful installation the load factor from the dynamo terminals may be approximately maintained at 100 per cent., and the variations need not exceed more than 1 or 2 per cent. or perhaps 5 per cent. in the most extreme cases. This variation would only be temporary, as the electrolyzers are cut out successively for removing the copper or for repairs. A set of one or two electrolyzers will usually be at hand to take the place of those temporarily cut out of the circuit, so that any variation of the load will be very small and only momentarily.

In electrodeposition of copper, water-power, if available, presents more than ordinary advantages as compared with most industrial enterprises. Outside of the expense for attendence, the cost for producing water-power for 24 hours in a day is not appreciably more than for 8 hours; whereas, if the power is generated with fuel, the cost for fuel for 24 hours, as approximately three times that for 8 hours.

Copper deposits are usually located in mountainous districts where fuel is expensive, but where, fortunately, water-power is frequently available.

Next to water-power, producer gas presents evident advantages. With an ordinarily good installation, 1 h. p.-hour can be developed with 1.5 lb. of good coal with producer gas, whereas from 3 to 4 lb. are required for steam under the same conditions. With cheap coal the advantages of producer gas over steam installations may not be so great, but with the price of coal ranging from $5.00 to $10.00 per ton, it may be a controlling factor.

Comparison of Steam- and Water-power Plants.—The following table by Dr. Cary T. Hutchison[1] gives the cost of energy with steam-power and water-power, in cents per kilowatt-hour, for steam- and water-power plants, a medium head hydro-electric generating and transmission plant being assumed in the latter case. These values are based on the assumption of a fixed annual charge of $13.60 per kilowatt plus an output charge of 0.5 cent per kilowatt-hour for the steam plant, and a fixed charge of $20.00 per kilowatt of demand on the water-power plant. As shown, at a high value of load factor, the hydro-electric plants can show a much larger profit than the stream plants, while the profits decrease as the load factor becomes less.

In the last column of the table is shown the price at various load factors, at which energy from the hydro-electric plant must be sold in order to produce a profit of 6 per cent. on the investment.

COST AND SELLING PRICE OF ENERGY PER K. W.-HOUR AT VARIOUS LOAD FACTORS

Per cent. load factor	Cost of k. w.-hour in cents		Selling price water-power
	Steam-plant	Water-plant	
15	1.54	1.52	2.44
25	1.12	0.91	1.46
35	0.97	0.69	1.10
40	0.89	0.57	0.92
50	0.81	0.46	0.73
60	0.76	0.38	0.61
75	0.71	0.31	0.49

The above figures, while apparently high, are undoubtedly correct for the average hydro-electric power and transmission plant. Under special conditions where the hydraulic development is easy and no transmission line is required, they could be materially reduced.

Water-power can frequently be acquired and cheaply developed in the western part of North and South America, within transmitable distance from copper deposits. Under ordinarily favorable conditions such power should be generated at a cost of not exceeding $25.00 per kilowatt-year. Under extremely favorable conditions water-power may be developed very cheaply, as for instance in Norway, where it is produced at a cost of as low as $5.00 per horse-power-year. The Braden

[1] American Inst. *Electrical Engineers*, Dec. 16, 1909.

Copper Co. in Chile, has a plant of 1000 h. p. on the ground, to operate under a 1000-ft. head. The cost for power during the first 12 months of operation was less than $2.00 per horse-power-year, without figuring interest and depreciation. There were practically no repairs of any kind, and two Chileans attended the water wheels and dynamos.

Cost of Water-power in the Western United States.—Norman Read[1] estimates that with an average installation in the West, the cost of a hydro-electric plant of 1000 kilowatt capacity will be $150.00 per kilowatt. This will include head works, pipe line, machinery, building and a short transmission line.

Based on this cost of $150,000 the annual fixed charges and operating expenses will be as follows:

Fixed Charges:	
Interest, 6 per cent. on $150,000,	$9,000
Taxes, etc., 1/2 per cent.,	750
Average depreciation and obsolescence, 3.8 per cent.,	5,700
	$15,450
Operation and Maintenance:	
Operators, salaries,	$1,200
Oil, waste and supplies,	2,000
Contingencies,	500
	$6,700
Total annual costs,	$22,150

Basing the output on a 24-hour load, 80 per cent. load factor, the annual output will be 7,008,000. k. w-hours, which gives a total cost of slightly over 0.3 cent per kilowatt-hour, or about $26.00 per kilowatt-year.

Supposing, however, that in the year's operation the actual output of the plant is only 50 per cent. of its total capacity; in other words it has only a 50 per cent. load factor, then the annual output will be 4,380,000 kilowatt-hours. The fixed charges will remain the same, but it is probable that the operation costs will be reduced to $5500, making a total of $20,950, or slightly over 0.47 of a cent per kilowatt-hour.

In the East, $15.00 per kilowatt-year at the electrolyzer terminals may be considered a fair average price for cheap water-power. The selling price of power at Niagara Falls varies from $8.00 per horse-power-year for those buying only the water rights and putting in their own machinery, to $20.00 and $25.00 per horse-power-year for those buying the working current, adapted for their particular use. In Buffalo the cost of Niagara Falls Power in lots of 500 h. p. or over, is $27.50 per horse-

[1] Private communication from Mr. Read, Eng., Hug Water Wheel Co.

power-year, which converted to direct-current at 87 per cent. efficiency, equals $31.60.

The cost of installing water-power under favorable conditions, as for example in Norway, Sweden, or the western slope of the Andes, is illustrated by the following installations in Norway and Sweden.

COST OF WATER-POWER DEVELOPMENT IN NORWAY AND SWEDEN

	Turbine horse-power	Feet head	Cost per electric horse-power
Joesefors, Sweden	1,800	26	$70.00
Frykfors, Sweden	4,000	27	64.00
Yngeresdsfors, Sweden	8,250	60	38.00
Vamafos, Norway	75,000	86	26.00
Tya, Norway	73,000	3,290	36.00

Comparison of Steam and Producer Plants.—William O. Webber[1] gives the following costs of steam and producer gas installations, per horse-power. In this table the cost of the land, the buildings and the generator have been excluded, but all the auxiliaries together with the cost of foundations, setting, piping, cartage, freight and all other items which go to make up the initial cost of a complete plant have been included.

Horse-power of plant	Cost of steam-plant	Cost of gas producer—Vertical gas engine plant	
		Belted	Direct conected
34	$100	$132	$150
60	90	99	112
100	85	76	88
140	80	69	76
190	75	68	73
280	70	68	76
380	65	68	73
420	63	69	75
500	62		84[2]
620	60		86[2]
1,000	65		90[2]

[2] Horizontal.

[1] *The Iron Age*, March 16, 1911.

With reference to the comparative weights per horse-power of gas and steam engines, the following figures may prove of interest.

Horse-power	Pounds per horse-power	
	Vertical gas engines	Direct-connected Corliss steam engines
60	240 lb.	148 lb.
140	275	143
190	280	140
300	290	140
500[1]	300	250
750	300	213
1,000	340	213
1,200	350	215
1,500	375	219
2,000	400	210
2,500	400	250
3,985	400	270

[1] Horizontal.

Webber also gives the following cost of operation, expressed in dollars per horse-power-year, assuming fuel and labor to be the same for both types of plants; that is, coal at $5.00 a ton, whether used in steam boiler or in gas producer, and labor varying as given below. Fixed charges are also included in this table. The costs are given for 10 and for 24 hours operation per day.

COST OF POWER PER HORSE-POWER PER ANNUM

Horse-power	Labor	Steam engines		Gas-producer gas engines	
	10 hr.	10 hr.	24 hr.	10 hr.	24 hr.
20	$30.00	$146.00	$292.00	$75.00	$150.00
40	20.00	120.00	240.00	42.00	84.00
60	15.00	105.00	210.00	38.65	77.30
80	12.00	95.00	190.00	35.00	70.00
100	12.00	86.40	172.80	30.00	60.00
200	10.00	77.10	154.20	27.00	54.00
300	8.60	69.22	138.44	25.00	50.00
400	7.25	61.90	123.80	24.50	49.00
500	6.20	55.29	110.58	24.00	48.00
600	5.40	49.28	98.56	23.50	47.00
700	4.70	43.79	87.58	23.00	46.00
800	4.15	39.73	79.46	22.50	45.00
900	3.75	34.05	68.10	22.00	44.00
1,000	3.50	29.80	59.60	21.50	43.00
1,500	3.25	25.77	51.54	18.75	37.50
2,000	3.00	21.75	43.50	17.25	34.50

"In gas-producer gas engine plants operating 10 hours per day the coal consumption varies from 1 lb. in the largest sizes, to 2 1/2 lb. per horse-power per hour in the smaller sizes, while in steam-plants this figure will vary from 12 lb. in a small 20-h. p. plant to 7 lb. in a 100-h. p. plant, 5 lb. in a 500-h. p. plant, 2 1/2 lb. in a 1000-h. p. plant, and 2 lb. in a 2000-h. p. plant, where strict account is kept of all coal used throughout the 24 hours, including the banking of fires during the night and standover losses in both cases.

"The water consumption is practically the same in amount per horse-power for either gas-or steam-plant, that is, on the smaller sizes of gas engines, 5 gallons per engine horse-power per hour for the jacket water to probably about 4 gallons on the larger sizes, besides which a similar amount must be used in the producer per horse-power for washing purposes. The steam-plant uses about 5 gallons of water per horse-power per hour for the simple plant down to 3 gallons per horse-power per hour on a condensing engine of 200 or 300 h. p. or over for the generation of steam. In condensing plants, approximately 26 times the water used by the engine is required for the condenser."

Tests made by the U. S. Geological Survey, with producer gas, 168 in all, include 138 on bituminous coals, 9 on sub-bituminous coals, 10 on lignite, and 11 on miscellaneous fuel. The average consumption of fuel for a brake-horse-power-hour was 1.36 lb. of bituminous coal; 1.99 lb. of lignite; the minimum consumption was 0.84 and 1.48 respectively. Comparative tests of 75 bituminous coals under a water tube boiler and in gas producer showed that the average fuel consumption per brake-horse-power in the steam-plant was 2.7 times that in the producer plant. Several low-grade lignites that were of little value or even worthless, under the steam boiler, gave excellent results in the producer.

There are a great many producer-gas power-plants in operation in the United States, ranging in size from 15 to 6000 h. p. About 88 per cent. of these are running on anthracite coal, a few on coke, and the remainder on bituminous coal and lignite. There has been considerable difficulty in applying the producer engines to the inferior qualities of coal, but these difficulties are being overcome, and plants are now in successful operation even on inferior quality of lignite.

Producer-gas Plant using Western Lignite.—Lignite is quite generally distributed throughout the western part of the United States, and is quite common in many other countries. Its calorific value under a steam boiler is quite low; used in a gas producer its value is enormously enhanced. The Western Chemical Manufacturing Co., Denver, Colorado, for some years have been generating their power from western lignite with gratifying results. According to Lewis B. Skinner,[1] Supt. of the Company, "The machines are practically continuous (demanding 24 hours service, 365 days in the year); they are automatic, the ashes are removed and fires barred during running; they are economical of labor,

[1] *Western Chemist and Metallurgist*, July, 1909.

one man per shift taking care of three 175 h. p. each; they are efficient, test runs showing a consumption of 1.6 lb. of lignite of 9250 b. t. u. value per brake-horse-power, and 1 1/4 lb. of bituminous coal of 11,500 b. t. u. value for average load; good gas is produced running about 120 b. t. u. per cubic foot using low factors; the gas is practically tarless, containing from 0.01 to 0.02 gr. per cubic foot, of lamp black and tar."

The consumption of fuel in a gas engine running at its rated load when natural gas is used, is from 13 to 17 cu. ft. per b. h. p. per hour; with coal gas, 15 to 19 cu. ft. per b. h. p. per hour, and with producer gas about 1 1/4 lb. of coal per b. h. p. per hour. These are average good results; large engines show higher economy than smaller engines and have given 1 b. h. p. with a consumption of 1 lb. of coal per hour.

The efficiency of a steam-plant is largely decreasing at low load and overload, while the economy of a gas producer remains constant within wide limits. Gas engines show the greatest economy at full loads, while steam engines have it below this point.

Cost of Power with Steam-plants.—Much depends on the installation. If the power is installed in reasonably large units, as it would be in a copper extraction plant where the metal is electrolytically deposited, only a compound condensing engine should be considered.

The following tables by Wm. E. Snow[1] give the essential data in reference to steam-power compound, condensing, power-plants, in sizes ranging from 100 to 2000 horse-power.

Oil Engines.—It frequently happens, as in the arid regions of the United States and Mexico, that neither coal nor water-power are cheaply available, but that oil can be obtained at a price which is not prohibitive. If oil is used for power purposes, it is best to use it direct in internal combustion engines, rather than to fire the oil under a steam boiler.

Internal combustion engines, using oil, are in use in large installations in various parts of the world, and are made in sizes ranging from 25 to 4000 h. p., for stationary purposes. Results of tests with the Diesel engine show that the consumption of fuel oil is as low as 0.4 lb. per horse-power-hour in the larger and 0.46 lb. per horse-power-hour in the smaller sizes, and these figures are maintained in practice under working conditions. With oil at $10.00 per ton, the fuel costs are 0.2 cent for the larger, and 0.23 cent for the smaller sizes, per horse-power-hour. This low cost is not materially increased at light loads, as the efficiency of the Diesel engine is extremely well maintained at all loads.

At the Deadwood mine and mill in the Mogollon district, New Mexico, 125-h. p. De La Vergne, type F. H. oil engine has been in continuous operation for 12 months.[2] It is operated at an altitude of 7000 ft. A Prony brake test made when the engine was first installed showed

[1] *Engineering Magazine*, May, 1908.

[2] Earl C. Cleveland, *E. and M. J.*, April 6, 1912.

TABLE 6. ESTIMATED COST PER HORSE-POWERS OF STEAM-POWER PLANTS COMPLETE, COMPOUND CONDENSING

Horse-power of engine	100	200	300	400	500	600	700	800	900	1000	1500	2000
Steam per horse-power per hour, lb	24.1	22.3	20.2	19.5	19.	18.1	17.3	16.2	15.1	14.5	13.9	13.5
Coal per horse-power per hour, running time	2.75	2.45	2.40	2.35	2.30	2.25	2.20	2.15	2.10	1.95	1.80	1.75
Total coal per horse-power per hour	3.15	2.85	2.75	2.70	2.65	2.60	2.55	2.50	2.45	2.25	2.07	2.02
Boilers, including setting	$8.	$7.60	$7.40	$7.30	$7.25	$7.20	$7.15	$7.05	$6.90	$6.80	$6.60	$6.40
Flues	1.93	1.82	1.59	1.36	1.12	1.02	0.92	0.80	0.68	0.57	0.57	0.57
Stack	4.55	4.	3.65	3.30	3.08	2.95	2.90	2.85	2.80	2.75	2.70	2.68
Feed pumps	0.93	0.57	0.46	0.37	0.31	0.29	0.28	0.27	0.26	0.25	0.24	0.19
Engine and condenser	25.	24.	23.	22.	21.50	21.25	21.	20.75	20.50	20.25	19.50	19.
Engine foundation	5.70	5.60	5.50	5.40	5.30	5.20	5.10	5.	4.90	4.80	4.40	4.10
Piping	13.80	11.20	9.10	8.	7.40	6.80	6.50	6.25	6.	5.75	5.10	4.55
Heaters	2.85	2.55	2.25	2.	1.75	1.42	1.12	1.12	1.	1.	0.95	0.95
Boiler house	28.50	24.	11.20	8.	6.40	5.70	5.35	5.	4.68	4.55	4.10	3.96
Engine house	28.50	24.	11.20	9.35	8.50	7.20	6.20	5.60	5.35	5.	4.75	4.55
Coal pocket	5.70	4.	3.10	2.60	2.40	2.27	2.16	2.05	1.93	1.82	1.73	1.61
Incidentals	9.70	8.	6.80	6.50	6.25	6.	5.75	5.50	5.25	5.	4.75	4.60
Total cost per horse-power	106.60	93.30	86.20	76.20	71.20	67.30	64.40	62.20	59.30	55.70	54.40	53.20

TABLE 7. YEARLY COST OF STEAM POWER, 308 DAYS OF 10 HOURS PER DAY, COMPOUND CONDENSING

	1Man $16 per week	1 Man $16 1 Man $7	1 Man $16 1 Man $7	1 Man $16 1 Man $10 1 Man $7	1 Man $16 1 Man $13 1 Man $7	1 Man $17 1 Man $13 1 Man $10	1 Man $17 2 Men $22 1 Man $10	1 Man $18 2 Men $22 1 Man $10	1 Man $18 2 Men $25 1 Man $10	1 Man $19 2 Men $26 2 Men $20	1 Man $22 3 Men $36 2 Men $20	1 Man $25 4 Men $50 2 Men $20
Horse-power of engine.....	100	200	300	400	500	600	700	800	900	1000	1500	2000
Total coal per horse-power per hour, pounds.	2.75	2.45	2.40	2.35	2.30	2.25	2.20	2.15	2.10	2.00	1.80	1.75
Cost of plant per horse-power.	$105.60	$93.30	$86.20	$76.20	$71.20	$67.30	$64.40	$62.20	$59.30	$55.70	$54.40	$53.20
Fixed charges on plant at 11 per cent.	1160.00	2060.00	2850.00	3350.00	3920.00	4451.00	4952.00	5492.00	5910.00	6130.00	9000.00	11,880.00
Cost of coal at $5 per long ton.	1910.00	3370.00	5100.00	6700.00	8380.00	9650.00	11,000.00	12,500.00	14,300.00	14,500.00	18,600.00	24,200.00
Attendance.....	880.00	1220.00	1220.00	1760.00	1930.00	2100.00	2650.00	2700.00	2930.00	3480.00	4400.00	5200.00
Oil, waste and supplies.....	143.00	205.00	240.00	285.00	315.00	350.00	385.00	420.00	445.00	470.00	600.00	685.00
Total yearly cost, coal at $5 per ton.	4198.00	6948.00	9496.00	12,171.00	14,596.00	16,618.00	19,050.00	21,674.00	23,644.00	24,595.00	35,.00 100	42,018.00
Total yearly cost, coal at $4 per ton.	3780.00	6200.00	8550.00	11,000.00	13,200.00	15,700.00	17,200.00	19,500.00	21,200.00	22,200.00	31,500.00	37,800.00
Total yearly cost, coal at $3 per ton.	3300.00	5400.00	7500.00	9700.00	11,500.00	13,200.00	15,200.00	17,100.00	18,500.00	19,500.00	27,500.00	33,000.00
Yearly cost per horse-power, coal at $5 per ton.	42.20	35.10	31.50	30.50	29.20	27.70	27.30	26.10	25.20	24.50	23.50	21.00
Yearly cost per horse-power, coal at $4 per ton.	37.80	31.50	28.40	27.00	26.10	24.90	24.60	23.50	22.60	22.00	20.30	18.90
Yearly cost per horse-power, coal at $3 per ton.	33.20	27.70	25.00	23.80	23.00	21.90	21.50	20.60	19.90	19.40	17.90	16.60

a development of 125 h. p. and an oil consumption of 0.48 lb. per brake-horse-power-hour.

At this place 110 h. p. is used for 12 hours and 50 h. p. for the rest of the day making 1920 h. p.-hours per day. This requires, taken from a year's run, 860 lb. of fuel oil, or 0.45 lb. per horse-power-hour. Fuel oil from Kansas fields is used which costs at the railroad $1.72 per barrel of 42 gallons, and at the mine, 90 miles from the railroad, $5.46 per barrel, 13 cents per gallon, or 1.7 cents per pound. This figures out a cost of 0.778 cents per horse-power-hour, or $68.1 per horse-power per year, 24 hours' service for 365 days.

The gravity of the oil is 27° Beaume and its heating value is 19,000 b. t. u. One engineer on each shift looks after the entire plant.

Progress, in the use of oil for power purposes, has also been made along the lines of first converting the oil into producer gas, and then using it in gas engines.

CHAPTER XXI

ECONOMIC CONSIDERATIONS

Of the various hydrometallurgical methods used and suggested, the electrolytic processes appear to offer the greatest ultimate advantage. Chemical methods have been used for many years, but they do not adequately solve the problem. Nor have the electrolytic methods met with the success that was hoped for. There is this difference, however, that while the chemical methods do not appear to be susceptible to much further improvement, the electrolytic methods are at least theoretically adequate, and no process which is not theoretically adequate, can ever hope to achieve phenomenal commercial success.

In the extraction of copper from a suitable ore, by means of sulphuric acid as the solvent and iron as the precipitant, there is no chemical nor mechanical difficulty. The process is energetic and the results are positive. The cost of carrying out the process in copper-mining districts is prohibitive, because neither sulphuric acid nor iron are cheaply available.

On the other hand, electrolytic methods in which the copper is precipitated and the solvent regenerated by a cyclic process, the commercial advantages are adequate, but the technical difficulties have been serious. That these difficulties will be overcome, no one well informed will deny. Many of the defects in the earlier electrolytic processes have been surmounted and there is no reason why those still remaining should not succumb as the fundamental causes for the disturbances are better understood. When they have been overcome, the electrolytic processes will be almost as important a factor in the metallurgy of copper as the cyanide and chlorination processes are now in the metallurgy of gold and silver; no mixture of ores will be required, installations can be economically made and cheaply operated at the mines in any unit, and the product will be the metal or metals salable direct to the consumer. It is practically certain that with the proper working out of the electrolytic processes, pure electrolytic copper will be produced direct from the ore. This has already been accomplished on a commercial scale, and a general application of the electrolytic methods is reasonably within sight.

Small copper mines, and large ones in their incipiency, are rarely, if ever, located directly on a railroad, where acid and iron are cheaply available. Theoretically, it takes 1.66 lb. of ordinary commercial sulphuric acid of 66° B. to dissolve 1 lb. of copper and 0.95 lb. of cast iron to precipitate it. This represents the smallest possible amount of

treating the most favorable ores the consumption of commercial sulphuric acid is not likely to be less than 2 to 2.5 lb., per pound of copper extracted, and the consumption of scrap iron is not likely to be less than 1.5 to 2 lb. per pound of copper precipitated. Sulphuric acid could not be delivered at a mine, under ordinary conditions, for less than $25.00 to $40.00 per ton, and it would not cost much less to manufacture it on the ground in the small amounts required, especially if the ore is all oxidized and sulphur or sulphide ore is not cheaply available. Shipping acid is expensive, since it has to be handled in special containers, and these for wagon hauling are inconvenient. The containers, whether an iron tank on a railroad car, irom drums, or carboys, have to be returned empty at considerable expense, or paid for at considerable loss. Under the same conditions, iron at the plant will cost from $15.00 to $20.00 per ton, and the supply may be uncertain. Tin cans are not usually available; it takes a good many tin cans to make a ton of iron, and any local accumulation, either of tin cans or scrap iron, would soon be exhausted.

It is safe to conclude, therefore, that under the ordinary conditions of copper mining, the cost of acid and iron alone, per pound of copper, would be between 4 and 6 cents, even on ore well adapted to the process. All the iron and acid, once used, is irrecoverably lost. The cost of the acid and iron for a ton of copper, valued at say $250.00 would at 5 cents per pound of copper extracted be $100.00. This still leaves considerable margin if the other expenses are not too high.

It is evident that if the cost of acid and iron could be eliminated by a cyclic process, at the expense of cheap power and waste elements contained in the ore, and having electrolytic copper as the end product, the principal disturbing factor will have been removed. This is what is offered by electrolytic processes.

Cost of Depositing Copper Electrolytically.—The following table gives the theoretical cost, per ton of copper, at the stated price of power per kilowatt-year, figuring 360 days operation of 24 hours, for a year. It is assumed that the solvent is regenerated, as the copper is precipitated.

THEORETICAL COST OF ELECTROLYTIC PRECIPITATION, PER TON OF COPPER

Cost of power per kilowatt-year	Cupric sulphate	Cupric chloride	Cuprous chloride
$10.00	$1.08	$1.19	$0.63
25.00	2.70	2.98	1.57
50.00	5.40	5.95	3.14
75.00	8.10	8.94	4.71
100.00	10.80	11.19	6.28

In practical operation, an energy efficiency of only about 50 per cent. of the theoretical will ordinarily be realized, so that the cost of electrodeposition in practice, will be about double the above theoretical figures. Even under these conditions, $15.00 per ton of copper for electrolytic deposition and regeneration, would come well within the average limits. Under favorable conditions it would be less than $10.00 and might conceivably be as low as $2.00.

It has been proved conclusively both by practice and numerous experiments, that there is not the slightest difficulty in practice in depositing one pound of copper per kilowatt-hour, with the regeneration of the combined acid. Under these conditions the cost of power for deposition and regeneration would be as follows:

COST OF DEPOSITION AND REGENERATION, PER TON OF COPPER, ON THE BASIS OF 1 LB. OF COPPER PER KILOWATT-HOUR

Cost of power per kilowatt-year	Cost per ton of copper
$10.00	$2.31
25.00	5.80
50.00	11.34
75.00	17.34
100.00	22.68

On the other hand, both the theoretical and practical costs above given may be greatly reduced by taking into account the e. m. f. due to the anode reactions. With low current densities this is largely realized, as in the Siemens-Halske and Hoepfner processes, where the theoretical voltage is less than 0.5 volt and the practical voltage is given as 0.8 volt. On this basis the cost of precipitation and regeneration would be remarkably low as shown by the following table:

COST OF DEPOSITION AND REGENERATION, PER TON OF COPPER

Cost of power per kilowatt-year	Siemens-Halske process		Hoepfner process	
	Theoretical 0.36 volt	Actual 0.8 volt	Theoretical 0.18 volt	Actual 0.8 volt
$10.	$0.33	$0.88	$0.08	$0.44
25.00	0.83	2.18	0.20	1.09
50.00	1.66	4.34	0.40	2.17
75.00	2.79	6.42	0.60	3.26
100.00	3.32	8.70	0.80	4.35

In these figures, 90 per cent. is allowed for the current efficiency for the actual working, and 100 per cent. for the theoretical, which is

taken as the voltage required for decomposition based on the molecular heats of combination.

With processes in which the anode reactions are more positive than those in the Siemens-Halske and Hoepfner processes, as for example, those in which sulphur dioxide is used as a depolarizing agent, a still greater theoretical reduction is possible than the costs above given. Taking for example the electrolysis of copper sulphate solution with sulphur dioxide as a depolarizing agent, the sum total of the reactions may be expressed:

$$CuSO_4 + SO_2 + 2H_2O = Cu + 2H_2SO_4 + 7300 \text{ calories},$$

which amounts to 0.16 volt acting in the direction of the current or as a battery. In this case copper is theoretically deposited without the application of external power, the same as in the iron-copper or iron-coke couple. Tosizza ascertained that the transformation of the sulphurous acid into sulphuric acid at the anode gives rise to an electromotive force which diminishes the necessary voltage and lowers it to 0.2 volt, and obtained a deposit of pure electrolytic copper directly from an impure solution, with a sufficient intensity, at an electromotive force of about 0.6 volt. The conditions are somewhat similar when sulphur dioxide is used as a depolarizer in the electrolysis of cuprous chloride.

Such voltages would bring the cost of deposition down to a very small item of the total expense, but it is only with low current densities that such results can be realized. Still, where power is expensive, it would certainly be advisable to work with low current densities at the sacrifice of other considerations.

Comparison of Electrolytic Methods with the Iron Precipitation Process, Using Sulphuric Acid as the Solvent.—It may be assumed that the cost of acid in small installations is about $25.00 per ton, and the cost of iron $15.00 per ton, at the mine, and that it will take 2.5 lb. of acid to dissolve 1 lb. of copper from the ore and 1.75 lb. of iron to precipitate it. Power may be assumed at $75.00 per kilowatt-year, and the rate of deposition 1 lb. of copper per kilowatt-hour.

Cost of Acid and Iron, per ton of Copper	
Acid, 5000 lb., at $25.00 per ton,	$62.50
Iron, 3500 lb., at $15.00 per ton,	26.25
	$88.75
Cost of Electrolytic Deposition, per Ton of Copper	
Power, $75.00 per kilowatt-year,	$17.34
Acid, *credit;* assuming a 90 per cent. anode efficiency there is regenerated 1.5 tons of acid in the deposition of 1 ton of copper, valued at,	37.50
Credit,	$20.16
The total difference, therefore, in favor of the electrolytic process, per ton of copper is	108.91

It is also assumed that the cost of operation is the same; while in the electrolytic process some allowance must be made for disintegration of anodes and diaphragms, this is considered as compensation for the very impure copper obtained with iron precipitation, and the greater expense for accumulation of copper and handling of iron after its delivery at the mine.

From all of the above figures it will be seen that the electrolytic processes offer enormous economic possibilities, especially when it is considered that the cost, under favorable conditions, is not much greater than the refining of blister copper when the blister copper has to be remelted and cast into anodes.

In electrolytic installations the plant, when taken as a whole seems very large, but the cost of power is low when reduced to the basis of a pound or a ton of copper extracted.

Economic Relation of Current Density and Voltage.—The economic relation of current density and voltage may be illustrated from the following results recorded in electrolyzing a copper sulphate solution:

RELATION OF CURRENT DENSITY TO VOLTAGE

Amperes per square foot	Recorded voltage	Pounds of copper per kilowatt-hour	Cost of power, per ton of copper. Power at $75.00 per kilowatt-year
10	1.5	1.74	$10.00
20	2.2	1.19	14.59
40	3.5	0.75	23.76
60	5.0	0.52	33.33

From these results it follows that while six times as much copper is deposited in a given time, at 60 amperes per square foot as at 10, it takes three and one-third times the power, per pound of copper, to deposit it. If power is expensive, the lower current density would be preferable, but as the power becomes cheaper, it would doubtless be economy to increase the current density, and reduce other factors in the total cost of treatment.

Aside from the electrolytic precipitation, and regeneration of the solvent, the electrolytic methods are not essentially different from chemical methods, and on ores adapted to either, a purely chemical or electrolytic process, offers no more difficulty than is ordinarily met with in any of the solvent processes.

It is evident that a process to be operated on a large scale must have an energetic solvent as the basis. Many processes, both chemical and electrolytic, have failed on account of the indifferent nature of the solvent used. This was the greatest difficulty with both the Hoepfner and Siemens-Halske processes, and a difficulty which in those processes

would appear to be insurmountable. The anode and diaphragm difficulties that Hoepfner had have since been surmounted. A diaphragm working under the conditions of either the Siemens-Halske or Hoepfner processes, where the ferric and ferrous sulphates, and the cupric and cuprous chlorides are separated by a diaphragm, is in no wise so difficult a problem as that encountered in the electrolysis of salt, where a diaphragm separates an acid anolyte from a highly caustic catholyte; and the electrolysis of salt, under these conditions, is now carried on with enormous installations in various parts of the United States and Europe in the manufacture of caustic soda and chlorine compounds.

Chemical Treatment of Sulphide Ores.—When economic conditions are favorable to the treatment of copper sulphide ores, as for example the treatment of cupriferous pyritic cinder by the Longmaid-Henderson process in large industrial centers, the advantages of electrolytic over purely chemical methods, are not so marked. Under such conditions sulphuric acid is cheaply available and iron can be bought at a low figure with a dependable supply. But if acid and iron are cheaper under such conditions than in remote mining districts, power would also be cheaper, but the difference would not be so great.

Sulphide ores are as amenable to wet methods as oxidized ores, although the cost of treatment may be a little greater, due to roasting. But roasting is not an evil without some compensation. If the roasting is carefully done, much of the copper may be made soluble in water, and thus reduce the amount of acid required, or avoid its direct purchase or manufacture. The sulphurous gases from the roasting furnaces may be used to manufacture acid to treat oxidized ores, or they may be used by a regenerative method and converted into acid without the installation of a costly acid plant. If a regenerative process is used, as for example those based on electrolysis or hydrogen sulphide, only about half the acid need be manufactured; or for the same output of acid about twice the amount of ore can be treated.

Sulphide ores, after roasting, will usually not consume as much acid as similar oxidized ores, because many of the injurious elements are rendered harmless by roasting. The percentage of extraction of the copper in roasted ores is not likely to be as high as in oxidized ores. Low-grade sulphide ores are ordinarily amenable to concentration; if a reasonably satisfactory recovery can be made in this way, it will usually be advisable to roughly concentrate the low-grade ore and then treat the low-grade concentrate by roasting and a solvent process. Under such conditions, if a regenerative method is used, no acid need be provided, and no fouling of solutions need occur. The process is simplified and the cost of installation, for the same output will be comparatively small. It is always better to work with more or less concentrated solutions than with lean copper solutions; the regeneration in a regenerative

process will be the same, per pound of copper, but the consumption of acid, per pound of copper extracted, will be materially less.

It will readily be seen that if a sulphide ore is roasted so as to make about 50 per cent. of the copper soluble in water, the remainder of the copper may be extracted with the regenerated acid, and in this respect sulphide ores present advantages over oxidized ores in the wet treatment.

Comparison of Wet Methods with Smelting.—With the exception of the output of the Lake Superior region, practically all the copper produced at the present time is smelted from its ores into matte. The matte is converted into blister copper, and the blister copper is then electrolytically refined to produce the marketable electrolytic copper. In most of the smaller independent smelting plants matte is the end product of the local metallurgical treatment.

Copper ores, as a rule, are not self-fluxing, and many ores do not contain sufficient sulphur to produce a suitable matte. Not infrequently sulphide ores are hauled several hundred miles to provide the sulphur necessary for matte when smelting oxidized ores.

For smelting, under ordinary conditions, there may be required, in addition to the ore if the ore is oxidized and silicious, coke, iron, limestone, and sulphur. Coke is rarely available in close proximity to copper mines, and as on the average of 10 per cent. coke is required for blast furnace smelting, the item of fuel becomes expensive unless the smelter is favorably located. While coke is not necessary in reverberatory smelting, more fuel is required than in blast furnace smelting, approximating 30 per cent. of the furnace charge. Iron and limestone, for fluxing purposes, are frequently found at no great distance from copper deposits, but these fluxes are usually barren of metal values, and if barren, act as a dilutant of the ore and add extra expense to smelting.

At the smaller smelters, converters are not usually installed to transform the copper matte into blister copper. Under such conditions, smelting is simply a method of concentration. The resulting matte, containing from 30 per cent. to 50 per cent. copper, has to be shipped to the refining companies. The end product of the smaller mines and smaller smelting companies is not, therefore, a salable commodity in the open market. No mine or smelting plant producing copper matte can, under such conditions, be considered an independent producer.

Smelting, while generally considered a universal process, nevertheless has its limitations, as well as the wet methods, and these limitations are economic and not technical. That smelting is very far from being generally applicable is evidenced by the fact that practically all the copper is now produced in a comparatively few centralized plants. Almost all attempts to profitably apply smelting on a small scale, or to highly silicious ores have met with disastrous results. And there is no lack of ore for small smelting installations if it could be successfully

accomplished, as is further evidenced by the shipments of large quantities of custom ores to the large centralized smelting plants.

Any ore can be smelted, but it is not always advisable or profitable to do so. Any ore can be treated by a chemical process and with a high recovery of the copper and precious metals but, like smelting, economic considerations are the guiding factors. The whole thing resolves itself down to a matter of cost per ton of ore treated or per pound of copper produced. If the ore is a sulphide and contains sufficient iron and lime for fluxing, and sufficient sulphur for a suitable matte, conditions are ideal for smelting if the price of fuel is not prohibitive. If the ore is oxidized and silicious, smelting is usually prohibitive on account of cost, but such conditions are ideal for chemical methods and the item of fuel is not so much a controlling factor.

Unless a chemical process can be devised to profitably treat the ores from the smaller mines, the only alternative for such mines is in smelting to a copper matte, or shipping to the larger smelting companies. But what the burden of shipping means may be known by the following treatment rate, in carload lots, from one of the large smelting companies, on an Arizona ore, having the following analysis:

Gold,	$2.70.
Silver,	18.0 oz.
Copper,	21.0 per cent.
Silica,	68.0 per cent.
Iron,	5.0 per cent.
Lime,	1.0 per cent.
Manganese,	1.0 per cent.
Carbon dioxide,	2.0 per cent.
Insoluble,	2.0 per cent.

Payments

"Gold: If 0.10 oz. or more contained, $19.00 per oz.

"Silver: If 1.0 oz. or more contained, 95 per cent. New York quotation.

"Copper: If 3 per cent. wet assay, or more contained, 90 per cent. of full wet assay at the quotation for electrolytic cathodes, less 3 cents per pound.

"Iron: Pay for all metallic iron (Fe) at 5 cents per unit.

"Lime (CaO): If 3 per cent. contained, all at 6 cents per unit."

Deductions

"Insoluble: All at 10 cents per unit.

"Zinc: 5 per cent. free; excess at 50 cents per unit.

"Arsenic, antimony, bismuth; 3 per cent. excess at 50 cents per unit."

Treatment

"F. o. b. smelter, on basis of 3 per cent. copper wet assay, per 2000 lb., $3.00. Deduct 10 cents for each per cent. of copper contained in excess of 3 per cent.

"Moisture: Minimum, 1 per cent.

"Bricking charge: Add $1.50 per ton to treatment charge when any lot contains concentrates or fines of which 25 per cent. will pass through a screen with openings 1/4 in. square.

"Sampling: On lots under two tons, $3.00 per lot."

Taking these rates on this silicious ore, we find that the actual value of the metals in the ore is $66.30. The smelter deductions from this metal value amount to $18.63. There is a credit of $0.25 for the 5 per cent. iron, and a deduction of $7.00 for 70 per cent. insoluble. The quoted treatment charge is $1.30 per ton. Therefore the full smelting value of the ore is $66.93. It costs $8.00 per ton for freight and cartage to get this ore to the smelter, to say nothing of sampling charges and expenses incidental thereto. Therefore the total expense and deductions for shipping this ore is not less than $34.93 per ton, although the nominal smelting charge is only $1.30.

This ore, which is typical of numerous deposits in the Western United States and in other countries, shows why many mines are unproductive and unprofitable, under existing conditions of smelting. The hope lies in the hydrometallurgical processes, and there should be no difficulty in treating this character of ore by a wet method, at a cost of not exceeding $5. to $6. per ton, especially if there is cheap water-power available in close proximity to the mine.

Oxidized ores are best adapted to any solvent process. It does not follow, however, that sulphide ores cannot be treated successfully or economically by wet methods. With the exception of certain chalcocite deposits no process has yet been made public which offers a probability of successfully treating sulphide ore without roasting. To decompose large quantities of sulphide ore, as would be necessary in large installations, by chemical methods, is a serious undertaking.

Roasting is no longer the expensive operation it once was. A perfect roast is neither required nor desired in copper extraction by wet methods. A perfect elimination of the sulphur would be fatal to the success of the operation. Roasting, for smelting work, is now regularly done for 25 cents a ton of ore, and there is no reason why, in a fairly large installation, roasting for a solvent process should not be done for from 40 to 50 cents a ton under similar conditions. The question might then arise, if roasting is necessary, and fuel is required for roasting, why not smelt? Even assuming that roasting requires as much fuel as blast furnace smelting, the fact still remains that any available fuel may be used in roasting, while in smelting coke is desirable, even if not absolutely necessary. Furthermore, in smelting, fluxes have to be provided, and the copper matte produced is no more salable in the open market than a good quality of ore.

If the ore is highly suited for smelting, it would be unwise to advocate

a chemical method. All ores are not adapted to smelting, neither are all ores adapted to chemical methods, and the wise course for the metallurgist to pursue is to work within the limitations of the process under consideration.

The nature of the solvent has much to do with the limitations of the process. Acid solvents are the only ones which have met with much encouragement from a technical point of view. Copper is somewhat soluble in many of the alkali solutions, but the alkali solvents present great difficulties, especially if electrolysis is to be made the basis of the process. If copper ores contain sufficient lime to seriously interfere with an acid process, it is a question to what extent a wet method would present advantages over smelting, when the ore contains much of the matter for a suitable fluxing mixture. Nevertheless, even with a suitable alkaline solvent there would be a wide field on ores containing much lime or magnesia. Iron need not present any great difficulties either with an acid or alkaline solvent. The fixation of atmospheric nitrogen, either as nitric acid or ammonia, may ultimately result in a successful method of dissolving copper from its ores. Nitric acid presents serious difficulties, however, both as to solution of the copper and as to its precipitation if a regenerative scheme is contemplated. Ammonia is more likely to result in a successful process than nitric acid; it has the disadvantage of being an exceedingly volatile gas, and would require special apparatus in its manipulation.

Hydrometallurgical plants for the treatment of copper ores will cost about the same as cyanide or chlorination installations of the same capacity, for the treatment of gold and silver ores, and will vary from $1.50 to $3.50 per ton, based on the yearly capacity. The cheapest installation that can be made is an ordinary sulphuric acid leaching plant, with iron precipitation, treating oxidized ores. If the ore is a sulphide and has to be roasted, or if the acid for leaching is to be made on the ground, the cost will be materially increased.

Electrolytic installations are more expensive on account of the large amount of power required, but the operating cost will be much less. The most expensive plant would be one treating sulphide ores, in which the material has to be roasted, and the copper is recovered by electrolysis.

In the matter of installation, therefore, the expense will not be materially different from cyanide or chlorination plants under the same conditions, but it will usually be somewhat less than smelting plants.

According to Ingalls[1] a blast furnace plant employing the semipyritic process, where no roasting furnaces are required, costs $600,000 for 330,000 tons annual capacity, or about $1.70 per ton. The Balaklala works, in Shasta County, California, where roasting is

[1] *E. and M. J.*, July 2, 1910.

required, for an estimated capacity of 437,500 tons, the cost was a little less than $3.35 per ton. The Highland Boy works, near Salt Lake City, with a capacity of 300,000 tons, cost $972,676, which amounts to $3.26 per ton. The Garfield works, near Salt Lake City, with a capacity of 800,000 tons, cost $6,000,000 or $7.59 per ton.

All cost deductions, made in a general way, are of course subject to modifications, and the fact remains, that all plants to recover the value economically in the metallic condition, are expensive to install, and this is a generalization which is true, independent of any particular process employed.

Chemical and Mechanical Difficulties.—The mechanical difficulties in the treatment of copper ores by wet methods, need not be serious. They are somewhat greater than they are in cyanidation, largely on account of the corrosive nature of the solvents, due to which special apparatus is required, and also on account of the acid solutions which do not filter as readily as alkaline solvents. The difficulties, however, are not as great as in the time-honored chlorination process for the extraction of gold, where the solutions contain both acid and free chlorine, and of the two, the chlorine is by far the greater evil. But that these difficulties are not serious, is evidenced by the fact that in Cripple Creek alone, from 800 to 1000 tons of ore have been treated daily for many years with sulphuric acid and bleaching powder, resulting in the formation of a charge containing free acid, chlorine, and calcium sulphate slimes which do not increase its filtering qualities. Even under these conditions a charge of ten to twenty tons of ore is filtered in from two or three hours. If filtration is impracticable or undesirable, decantation may always be resorted to. If the ore is chemically adapted to a wet process, the mechanical conditions can readily be complied with, but if the ore presents serious chemical difficulties, it would be well to consider some other method of treatment. Fortunately the chemical difficulties may with certainty be determined in advance in the laboratory, or on a small working basis.

General Applicability of Hydrometallurgical Processes.—The prevailing idea, especially in metallurgical literature, seems to be that hydrometallurgical processes for extracting copper, are applicable only to low-grade ores. But why limit them to low-grade ores any more than smelting or any other method? There is no logical reason whatever why the wet methods should have any limitations, either as to the grade of the ore or its mineralogical composition, provided the process is chemically adapted. This adaption will, in its ultimate analysis, resolve itself down to the consumption of chemicals, the same as in chlorination, cyanidation, or smelting.

An ore may be so low grade as to preclude its profitable working by any method, and there is no reason why wet copper processes should

be an exception to the general rule. If an ore is ideally adapted to chemical treatment, as some self-fluxing ores are adapted to smelting, then such an ore, even though of very low grade, can be profitably treated, as for example, those of Stadtberge which showed only from 0.5 to 1.5 per cent. of copper. At the Gumeshevsky estate, in Russia, dump material is successfully treated on a large scale by leaching in which the copper recovered amounts to only 8.6 lb. per ton of ore; and this appears to be the record for profitable copper extraction from low-grade ores by any process.

Copper is one of the most readily soluble of all the metals, and one of the most readily precipitated either chemically or electrolytically. Theoretically, the solvent processes, especially the electrolytic processes, offer all that could be desired, on ores chemically adapted; close extraction, cheap deposition, copper in its metallic form, saving of the precious metals, the installation of plants at the mines which may be operated in any unit and without admixture of other ores or fluxes. With these theoretical advantages it is reasonable to suppose that the chemical methods will ultimately be in as general use for the extraction of copper as the cyanide and chlorination processes now are for the extraction of gold and silver.

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